SURFACTANT – POLYMER FLOODING FOR CHEMICAL ENHANCED OIL RECOVERY IN CARBONATE RESERVOIRS

BY

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Dedication

TO MY BELOVED PARENTS

MR. & Mrs. Maqbool Hussain Malik

TO MY BELOVED BROTHERS

Inkisar, Iftikhar, Abrar & Absar

TO MY FRIENDS AND PAKISTAN COMMUNITY

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LIST OF ABBREVIATIONS

EOR	:	Enhanced Oil Recovery
CEOR	:	Chemical Enhanced Oil Recovery
SP	:	Surfactant-Polymer
CMC	:	Critical Micelle Concentration
IFT	:	Interfacial Tension
PAM	:	Polyacrylamide
HPAM	:	Hydrolyzed Polyacrylamide
FT-IR	:	Fourier Transform Infrared Spectroscopy
TGA	:	Thermogravimetric Analysis
UV-vis	:	Ultraviolet-visible Spectroscopy
IC	:	Ion Chromatography

ABSTRACT

Full Name : IZHAR AHMED MALIK

Thesis Title : SURFACTANT – POLYMER (SP) FLOODING FOR EOR IN CARBONATE RESERVOIRS

Major Field : MASTER OF SCIENCE IN CHEMICAL ENGINEERING

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The objective of this work is to study the interactions between surfactants and polymers. Surfactants and polymers are used in Enhanced Oil Recovery to decrease interfacial tension between water and oil and increase the sweep efficiency by increasing the viscosity of water. Studies will be conducted for different formulations of the surfactant and polymer by varying different parameters. With the help of these results, we can optimize the particular formulation of SP system for specific conditions. The effect of different types of surfactants and polymer blends on rheology and thermal stability will also be investigated and the best system will be recommended. Salinity is the major factor affecting SP system and the optimum salinity will be determined for a particular SP system using phase behavior. Effect of temperature, pressure and shear rate will also be investigated. Interfacial tension experiment will help us to find optimum concentration of surfactant to be used in core flooding experiments. Core flooding experiments will give insight on how these chemicals will work in real conditions.

This work will help in selection of the best system for chemical enhanced oil recovery from carbonate and other reservoirs as it helps in understanding which system will perform best under specific conditions.

ملخص الرسالة

الاسم الكامل: إزهار احمد مالك

عنوان الرسالة: تأثير البوليمرات و خوافض التوتر السطحي على تعزيز إستخراج النفط من حقول النفط الكربونية

التخصص: هندسة كيميائية

تاريخ الدرجة العلمية: مارس 2014

يهدف هذا المشروع الى دراسة البوليمرات و خوافض التوتر السطحي في عمليات استخراج النفط. تعمل خوافض التوتر السطحي على خفض طاقة التوتر بين النفط و الماء بينما تعمل البوليمرات على زيادة لزوجة الماء و بالتالي زيادة استخراج النفط الخام. تم في هذه المشروع دراسة تركيبات مختلفة لمحلول البوليمر و خافض التوتر السطحي و دراسة تأثير التركيبات المختلفة على الخواص الريولوجية و مدى إستقرار تركيب البوليمر و خافض التوتر السطحي عند درجات حرارة عالية. تعتبر درجة الملوحة عامل مؤثر جدا على تركيب البوليمر و خافض التوتر السطحي حيث تم ايجاد درجة الملوحة الملائمة لتركيب البوليمر و خافض التوتر السطحي. تم كذلك دراسة تاثير كلا من درجة الحرارة و الضغط على تركيبات البوليمر و خافض التوتر السطحي. تم قياس طاقة التوتر السطحي بين النفط و الماء من خلال تغيير تركيز خافض التوتر السطحي و ايجاد التركيز الامثل للخافض في عمليات استخراج النفط. لدراسة تاثير التركيب تم استخراج النفط بواسطة ضخ تركيب البوليمر و خافض التوتر السطحي خلال تكوين النفط و ايجاد كمية النفط المنتج بعد عملية الضخ. سيساعد هذا المشروع على ايجاد التركيب الامثل في عمليات تعزيز استخراج النفط من حقول الكربونات.

CHAPTER 1

INTRODUCTION

Oil is the main source of energy in the world and its demand is increasing day by day as countries are developing new technologies which require more energy. Although the price of oil is also increasing with the demand but because of the limited alternative resources, oil consumption is still increasing. Oil reservoirs are depleting with time and new technologies are being introduced to recover more oil from these reservoirs. Generally, the recovery of oil is categorized into three main classes: Primary, Secondary and Tertiary. Primary recovery method is a natural recovery method in which the oil is pumped without using any alternative technology. In secondary oil recovery method, water is used to force the oil to come out to the surface. It was reported that only one third of the Original Oil in Place (OOIP) was recovered using these two methods and still two third of the oil remains to be recovered (Hirasaki et al., 2008). For the recovery of the residual oil, new techniques are being introduced which are named as Enhanced Oil Recovery. It has been contributing since last few decades and still it is continuously developing to introduce new efficient methods. It is a large field and contains many methods out of which three major methods are currently used all over the world, namely, Thermal, Chemical and Gas methods (Manrique et al., 2011). The contribution of these methods towards EOR is shown in Figure 1-1 (Baujon et al., 2011) summarizing all the projects from 1959 – 2010.

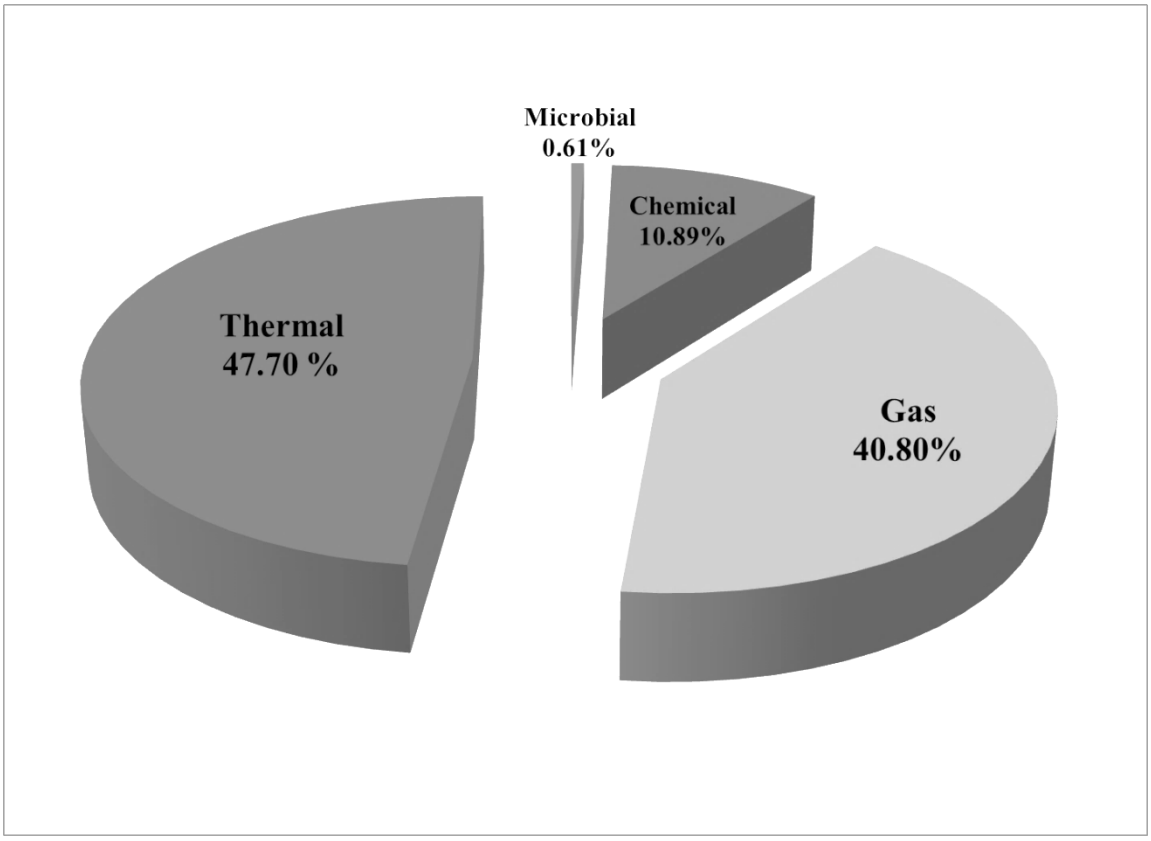


Figure 1-1 World EOR Data (1959-2010) 652 projects, 613 were reported by oil and gas journal, 39 were reported by SPE (Baujon et al., 2011)

Thermal Methods are used in sandstone reservoirs more effectively than in carbonate reservoirs. The purpose of this method is to use steam to reduce the viscosity of oil and make its flow easier. Cyclic steam method used the huff and puff method to inject steam and collect oil from the same well. This technique is used in Canada, US, Venezuela, Brazil and China (Manrique et al, 2011). There are additional classifications to this technique which are also playing role in EOR.

Gas Injection methods are used for the reservoirs containing light or volatile oil. It uses N_2, CO_2 or hydrocarbon gases. Amongst these methods CO_2 injection is the most widely used and applied method but it is limited due to the limited resources of gas.

In Chemical Methods, some chemicals like surfactants and polymers are introduced to enhance the sweep efficiency and reduce the interfacial tension of the oil to increase the overall efficiency. Up to 1980s, chemical EOR was at its peak but with the increasing prices of the chemicals, its application started decreasing. Most of the methods were applied in sandstone reservoirs and very few methods were reported for carbonate reservoirs (Needham & Doe, 1987). Now most of the projects of cEOR are running in China (Xiaoqin, 2009).

In chemical enhanced oil recovery (cEOR) surfactant, surfactant polymer (SP) and alkaline surfactant polymer (ASP) systems are used in order to extract residual oil from the reservoirs. Surfactants are used to enhance the flow of residual oil by generating a sufficiently low crude oil/water interfacial tension (IFT) to give a capillary number large enough to overcome capillary forces and allow the oil to flow. Surfactant also controls wettability, solubilization and emulsification properties by modifying the

interfaces involved. Since the viscosity of water is far less than that of oil, water is easy to penetrate when displacing the oil along the porous channels and viscous fingering may take place. To avoid viscous fingering, suitable polymers are added along with the surfactant which increase the viscosity of displacing fluid and decrease mobility ratio (Samanta, 2011). Polymers which are usually used for this purpose are hydrolysable polyacrylamide, polysaccharides, scleroglucan, polyvinylpyrrolidone, copolymer of N-Vinylpyrrolidone and acrylamide and polyvinyl amine (McCormick & Lowe, 2005). Some surfactants used for this purpose include internal olefin sulfonate, branched alkoxy based sulfonate and synthetic polyisobutylene.

Selection of the best method from the above mentioned methods is the main step in applying EOR in any area. For selecting the best technique, understanding of the reservoir conditions and behavior is very important as well as the role of economics. Shell has developed the curve showing the current status of all the techniques as shown in Figure 1-2.

Every method has its own significance but according to the prior work done on different methods, chemical EOR shows great potential for producing oil using much simpler technique. We shall use Chemical EOR method in our work. After developing the best formulation, it will be tested on lab scale and then it can be applied in the field after getting successful results on the lab scale.

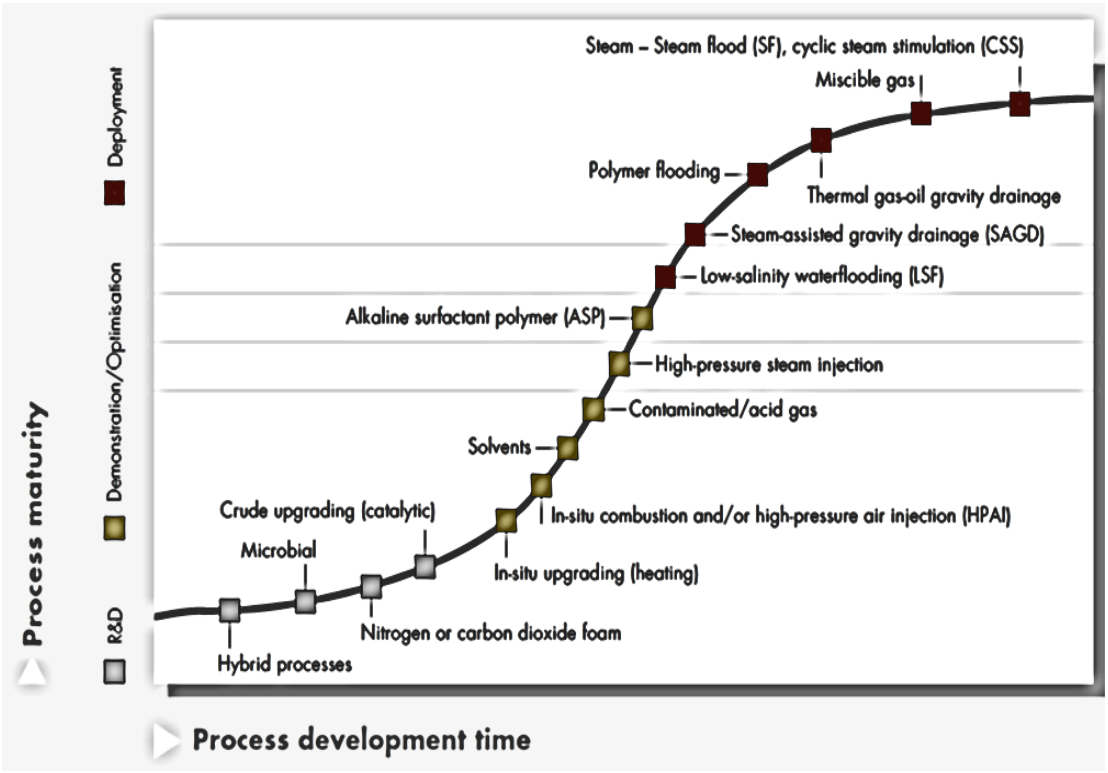


Figure 1-2 Recovery Techniques (Shell Global Solutions International)

Chemical EOR has great potential for producing oil using much simpler methods than other techniques. The major problem it was facing in past was the price of chemicals which was costing more than the oil produced, cEOR depleted in many fields. With increasing prices of oils and availability of various chemicals, cEOR is again considered as the major technique.

EOR techniques were mostly applied on sandstone reservoirs. Carbonate reservoirs usually show low porosity and may be fractured. These two properties lead to low recovery. In start thermal and gas flooding was applied mostly for carbonate reservoirs as these were producing more oil than compare to other techniques. With the passage of time new chemicals with much improved properties are introduced in the markets which are not totally analyzed for application of EOR. Many chemicals in pilot plant showed good signs of oil recovery which could help in boosting oil recovery using cEOR.

Chemicals used for cEOR had to be analyzed first on a lab scale under the same conditions of reservoirs and make sure that these could actually work in the field. For this purpose many experiments were designed like IFT, Phase Behavior and Core Flooding etc. Also rheology could also help in analyzing how chemicals will react when treated salts at high temperature and pressure.

Objectives:

The following are the objectives of this study:

- Study the chemical interactions of surfactant-polymer (SP) solution for EOR in carbonate reservoirs.
- Study the rheological properties of polymer, surfactant and SP solutions.
- Measure the interfacial tension for surfactant solutions and SP solutions.
- Study the effect of temperature on IFT, the thermal stability and the rheological properties of SP solution.
- Achieve the best SP formulation which has the ability to give the best sweep efficiency and low IFT values.
- Apply core flood experiments on selected SP systems.

Chapter 2

LITERATURE REVIEW

2.1 EOR in Carbonate Reservoirs

World's oil reservoirs are divided into two main categories of sandstone and carbonate. Mostly, projects are carried out in sandstone reservoirs. Half of the oil reservoirs are composed of carbonate rocks but only 18% of the projects are carried out on carbonate reservoirs (Manrique et al., 2010). To predict the future of oil and gas, it is necessary to develop techniques to recover the remaining 60% of oil from carbonate reservoirs (A Seethepalli et al., 2004). Several pilot tests have been carried out in Canada and US on carbonate reservoirs (Alvarez et al., 2008).

Carbonate reservoirs usually exhibit low porosity along with the oil – to – mixed wet rock properties and fractured structure which results in lower oil recovery. Thermal methods are not so efficient in the carbonate reservoirs, although some projects have used this method but its contribution is very small (Muci., 2011). Chemical EOR and particularly polymer flooding and gas injection are playing major roles in extracting oil from carbonate reservoirs. According to a survey by Manrique et al, 55% of the projects of carbonate reservoirs use gas injection technique, 40% use chemical EOR and remaining use thermal and other techniques. Although half of the oil remains of OOIP (Kiani, Wu., 2011) but still many projects are running and giving good results. In 1980s, many projects used cEOR in carbonate reservoirs and showed successful results. Vacuum field (New Mexico) was discovered in 1924 and started production in 1939 whereas

water flooding following polymer flooding started in 1983 which gives constant production of 3500 BOPD. Polymer solution was prepared using fresh water (387 ppm TDS) and polymer slug was injected at a concentration of 50 ppm. Production started declining in 1985 but it was reported as a successful project (Muci, Manrique., 2006)

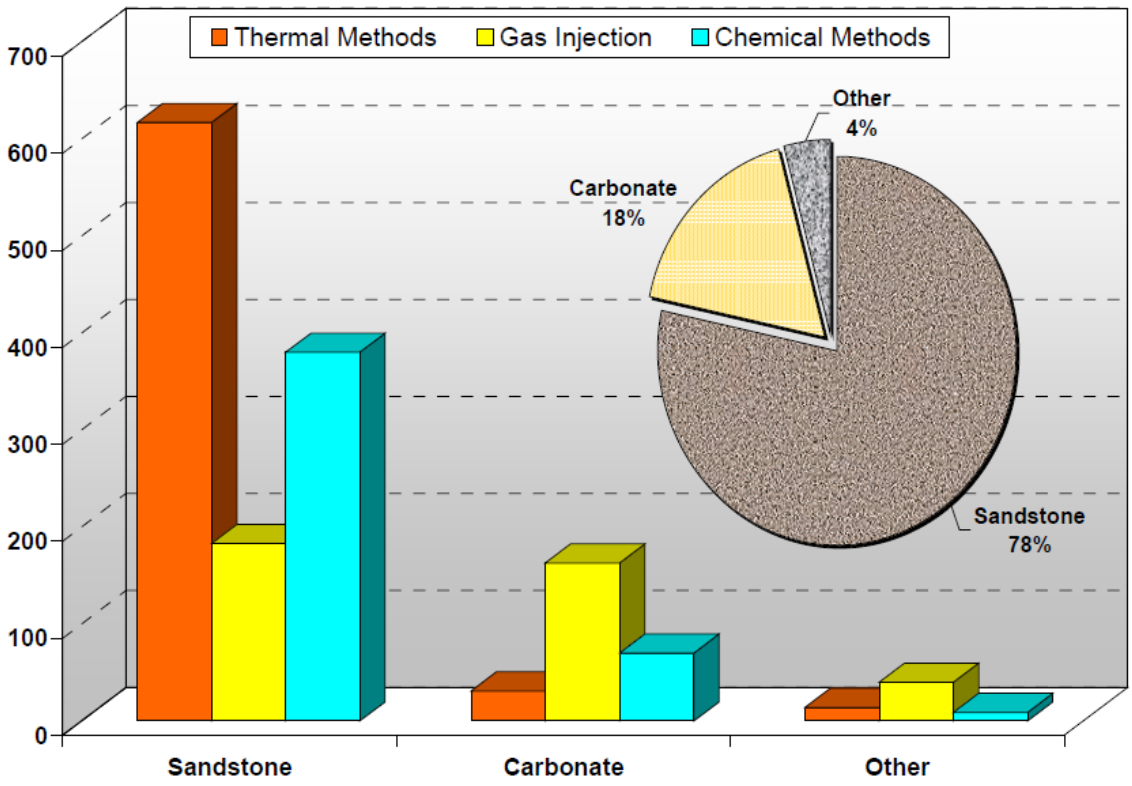


Figure 2-1 EOR field projects (Taber et al; based on 1507 international projects

2.2 Chemical Enhanced Oil Recovery

In the past few decades, a lot of research has been carried out on sandstone reservoirs and during 1980s, chemical EOR was at its peak but its application in carbonate reservoirs was not much preferred. Polymer flooding was applied in many projects and gave good results but with the time, due to high cost of chemicals as compared to oil, its use became limited and then finally depleted. But in the last decade, with paramount increase in the oil prices and demand of the oil, chemical EOR is again in business and new techniques are continuously being developed.

In chemical EOR, the basic principle is to increase the sweep efficiency and to reduce the interfacial tension between the oil and the water. For this purpose, surfactants are used. Surfactants are of many types e.g. Anionic, Cationic, and Non-Ionic etc. but usually they reduce the viscosity of solution; to increase the viscosity of the solution, polymers are used. Major classes of polymers which are used in the polymer flooding are Hydrolyzed Poly Acrylamides, Xanthum Gum, AMPS and some co-polymers. Salts are also added to get different values and to see the effect of salinity on the solutions. As the water used in cEOR is usually sea water so due to the presence of salts, SP systems are known as ASP systems in which Alkaline plays an important role in reducing the adsorption of surfactants on the rocks (Gao, Towler., 2010).

To select the best ASP system for cEOR, many properties had been studied using different techniques on the lab scale in order to select the best system that could be used in the field. Major test for polymers is to study the rheological behavior; for surfactants, change in the IFT is studied with and without the surfactant and the effect of the salt is studied in rheology, IFT and adsorption.

Polyacrylamide has been studied by many authors and its properties are well reported. In 1993, Shin and Cho studied its rheological properties against temperature and shear rate. They introduced temperature dependent viscosity equation based on Carreau Model. It considered the shear thinning non-newtonian characteristics and the temperature effect on the viscosity of polyacrylamide.

An aqueous solution of 0.1% PAM was prepared by dissolving pure PAM (Separan AP-273, Dow Chemical) in distilled water. Viscosity was measured using Brookfield Viscometer and water bath was used to control the temperature. First experiment was performed to measure the viscosity at three different temperatures by varying the shear rate. It was observed that zero-shear viscosity decreased significantly but apparent viscosity at intermediate and high shear rate did not decrease much. Second experiment was performed to measure the viscosity at four different shear rates and varying the temperature. It was observed that at high and intermediate shear rates, temperature had not much effect on the viscosity of the polymer, but at lower shear rate, temperature was the main factor to influence the viscosity and it had a strong effect on the viscosity.

Mamdouh T. Ghannam (1998) studied the effect of salts on the rheological behavior of polymer solutions. He used aqueous polyacrylamide solution (BDH Ltd.) and varied its concentration from 0.25 to 1wt %. He also varied the concentration of Sodium Chloride from 0.0 to 10 g/L and measured the viscosity and shear stress using RS 100 of Haake Rheometer. First he performed experiments to see the effect of shear rate on shear stress by changing the concentration of NaCl. His work shows the result that whether the

concentration of polymer was high or low, shear stress was reduced by increasing the concentration of NaCl.

Next experiment was performed to measure the viscosity against the shear rate. It was observed that as the concentration of NaCl is increased, the viscosity of the solution decreases both in case of lower PAM concentration and higher concentration. The viscosity decreased up to a critical shear rate and after this critical shear rate, it increased again and polymer showed a shear thickening behavior. This behavior was independent of the measuring device and was observed only in high molecular weight polymers. Critical shear rate for high concentration polymers was lower and the effect of NaCl was completely diminished as the concentration of PAM was increased.

The addition of NaCl to the PAM solutions decreased the shear stress and the viscosity. The effect of NaCl was less pronounced with concentration greater than 5 g/L. The viscosity of all the test solutions experienced the shear thickening behavior after a critical shear rate. For pure PAM solutions without salts, critical shear rate was observed to decrease with PAM concentration and the addition of salts increased the critical shear rate.

Seright and Mozley (2009) studied the thermal stability of HPAM and a copolymer. The major issue with HPAM was the hydrolysis which occurred at elevated temperatures in aqueous solutions. They arranged oxygen free and divalent cations free atmosphere setup. They checked the stability of HPAM with salts at different temperatures. They observed that in the absence of oxygen and free cations, the polymer can remain stable and can maintain half of its original viscosity for seven years at 100^{o}C

and for two years if kept at 120^{o}C. HPAM and copolymer AMPS (25%) was also studied which showed similar behavior and it was observed that it can also be used for the same purpose. Stability results showed same behavior with brines of 0.3% NaCl, 3% NaCl and 2% NaCl + 1% $NaHCO_3$. For solutions kept at 160^{o} C or higher temperatures, 2% NaCl + 1% $NaHCO_3$ showed the best results for stability than other brines. They didn't use any oxidants and showed the best stability results if there was no dissolved oxygen present in the water or oil. This study shows that the best results to use HPAM in enhanced oil recovery is up to the temperature of 120^{o}C if contact to the dissolved oxygen and free cations is reduced to a minimum value.

Zou and Zhao (2011) worked on modifying the PAM and made it suitable for enhanced oil recovery. They synthesized new polymers known as anionic acrylamide polymers and cationic acrylamide polymers. Both are copolymers and are studied using FTIR and SEM. These were prepared and studied for different polymerization conditions and optimum conditions were evaluated at which they gave the maximum results. It was observed that both of these polymers enhanced the thermal stability, increased the interfacial tension, showed greater resistance against the salts, increased the viscosity and gave better oil recovery than the original PAM. By the comprehensive study of these copolymers, it was observed that anionic polymer gave better interfacial properties and decreased the IFT whereas cationic polymer showed better resistance against salts and temperature. So for better stability and high temperatures, cationic copolymer is preferred and for lowering the IFT anionic copolymer is better to use.

PAM was mixed with cetyltrimethyl ammonium chloride(surfactant) to compare the IFT. Standard solution of 2 g/L of PAM and interfacial tension was measured in the

first experiment. Anionic copolymer showed the minimum IFT with the same surfactant, whereas the cationic copolymer showed better results than the original PAM but IFT was greater than anionic copolymer. As the concentration of surfactant was increased, IFT decreased but after a critical point it became stable because the interface became saturated after that point so no change in the IFT was observed after that point.

The temperature stability was also investigated and it was noticed that although viscosity was higher for anionic copolymer but with the increase in temperature, the decreasing rate was lower for cationic copolymer than anionic copolymer and the PAM was less efficient than both..

Similarly, viscosity against the concentration of polymer was measured and cationic copolymer showed the best results. From his work it was observed that after a particular concentration of polymer there is a sudden increase in the viscosity, this effect was due to the certain groups present in PAM which formed network structures after a certain concentration and increased the hydrodynamic volume due to which viscosification property increased.

Bataweel and Nasr-El-Din (2012) conducted a detailed study of maximum parameters that can affect the surfactant polymer solution in enhanced oil recovery. They studied the effect of surfactant on the polymer, salts effects and temperature effects. Amphoteric type surfactants were used in this study and it was observed that these surfactants were able to maintain the viscosity of the solution when mixed with sea water and no reduction was observed. They studied two polymer FLOPAAM 3630s with the molecular weight of 18×10^6 and a copolymer AMPS having molecular weight 6×10^6.

Both were provided by SNF. Surfactants used were betaine based amphoteric surfactants provided by Oil Chem and Alpha Olefin sulfonate provided by Stefan. HPHT Rheometer was used to study all the bulk rheological properties.

This work shows the effect of amphoteric surfactant concentration on the solution. As the concentration was increased, the surfactant viscosity increased when 6% NaCl Brine was added into the solution. The measurement was carried out at an atmospheric pressure and 75^{o}F.

Next experiment was carried out to see the effect of the salinity on the viscosity of the solution; it was observed that if surfactant and polymer concentrations were kept fixed and only the concentration of the salt was increased, the viscosity decreased. Also the cations decreased the viscosity of the polymer solution more than the anions. As the concentration of the polymer was increased, the viscosity was also found to increase.

This research work represents the result of the experiment which showed that without salts, surfactant has no effect on the polymer solution. Only in the presence of salts it causes variation in the viscosity but in absence of salts, viscosity almost remains constant.

In the presence of the salts, it was observed that amphoteric surfactant increased the viscosity; as the concentration of the surfactant was increased, the viscosity of the solution increased with or without polymer. Similarly other results for the decreased storage and loss modulus on addition of salts were also collected.

Taylor and Hisham (1995) conducted a research work on synthetic surfactant and its effects on crude oil/ alkali/polymer system. Polymer used was partially hydrolyzed

PAM and the degree of hydrolysis was 0.28 with the viscosity average molecular weight of 13 x 10^6 g/mol. Surfactant used was Neodol 25-3S with average degree of ethoxylation of 3 and average molecular weight of 439 g/mole and 60% active mass percentage. Apparent viscosity of various solutions was measured using a co-axial rotational viscometer at 30^{o}C. Sodium Carbonate was used as an alkali because it was found to be less reactive with the reservoir rock.

In this work one parameter shows that when the polymer concentration was increased, the viscosity also increased and the other parameter represents that as the concentration of the surfactant was increased, the viscosity was found to decrease. Surfactant has a very little effect on bulk properties and the changes are very small on bulk as compared to the polymer, the only change observed with the surfactant was the change in the IFT.

Viscosity decreased when the salt concentration was increased. Polymer and surfactant concentrations were kept fixed in these experiments.

Effect of surfactant concentration was observed on the IFT between oil and water. It was observed that as the concentration of surfactant was increased, the IFT of the solution decreased up to a certain limit. IFT after critical concentration started increasing. This critical concentration is called Critical Micelle Concentrations (CMC).

Shutang and Huabin (1995) developed alkali/surfactant/polymer (ASP) formulas in the Daqing oil field in 1995,.Each ASP solution gave interfacial tension (1FT) values in the range of 1 x 10^{-3} mN/m. Rheological studies with polyacrylamide polymers indicated that solution viscosity decreased with alkali addition, as well as the pseudo-

plasticity of the solution. Addition of surfactant to the alkali/polymer solution increased the solution viscosity with no slope change in the viscosity – vs – shear-rate plot. Incremental oil recovery was higher than that with water flood; 20% original oil in place (OOIP) increased for 0.2-PV ASP injection rate and 33% OOIP increased for 0.3-PV ASP injection rate for Daqing core. Surfactant and alkali retention were both less than 1 mg/g sand. The positive results of this laboratory study provided a fluid formula for a pilot ASP flood in the Daqing oil field.

Ma and Xia (2010) studied the effect of Alkali-Surfactant-Polymer on the rheological properties of the solutions. Effect of changing the concentration of the polymer, alkali types and concentration of alkali and its effect on rheological properties was studied. Haake RS 150 Rheometer was used to study the viscosity changes in the solution.

They studies the effect of alkali concentration, polymer concentration and surfactant concentration were fixed at 1 g/L and 0.03% at 45 C. Their work showed the results and the influence of the mass concentration of $NaCO_3$ and NaOH on the viscosity of ASP system. With the increase in mass concentration the viscosity was observed to decrease. For NaOH, decrease in the viscosity was following the same trend for all concentrations; $NaCO_3$ showed some unexpected results when the concentration was increased from 0.3% to 0.6%, a huge decrease in the viscosity were observed.

To study the effect of the polymer concentration on the ASP system, cocnetration of the surfactant and Sodium Carbonate was fixed at 0.03% and 0.3%, respectively. Experimentation was done at 45^{o}C and shear rate was varied. Polymer concentration was

varied from 0.5, 1 and 2 g/L. This study showed the increase in the viscosity as the concentration of polymer is increased gradually.

Zhao and Jackson (2008) presented results for high molecular weight internal olefin sulfonates (IOS) surfactants. These surfactants showed excellent performance results when tested using different crude oils that have made it difficult achieving high oil recovery with most surfactants already used in the past. High carbon number internal olefin sulfonates, when used with appropriate co-surfactants, co-solvents and alkali, gave those propoerties of phase behavior and ultra-low interfacial tension which are needed for maximum oil recovery. They showed that the performance of both SP system and ASP flooding can be dramatically improved at the same or less cost than with conventional surfactants and can be applied over a wider range of reservoir conditions. High carbon number internal olefin sulfonate surfactants showed good performance results at low concentrations and were found to be compatible with both polymers and alkali such as sodium carbonate when used with appropriate co-solvents. The extremely efficient approach for finding high performance surfactants, that were previously presented for light crude oils, has now been successfully extended to heavier crude oils. The identification of high-performance surfactants, that are suitable for high-temperature and paraffinic oil applications, opens the potential to recover a vast amount of additional oil outside the range of conditions considered practical in the past. The carbon number of IOS surfactants can be varied to apply it to difficult reservoir conditions, and co-surfactants can be coupled to improve surfactant slug design parameters (i.e. altering optimal salinity) and performance as well. The high performance and low consumption of

these surfactants when properly formulated makes them a more economical alternative to conventional surfactants.

Levitt and Jackson (2006) studied a number of promising EOR surfactants based upon a fast, low-cost laboratory screening process that was highly effective in selecting the best surfactants to be used with different crude oils. Initial selection of surfactants was based upon desirable surfactant structure. Phase behavior screening helped to quickly identify favorable surfactant formulations. Salinity scans were conducted to observe equilibration times, microemulsion viscosity, oil and water solubilization ratios and interfacial tension. Co-surfactants and co-solvents were included to minimize gels, liquid crystals and macroemulsions and to promote rapid equilibration to low-viscosity microemulsions. Branched alcohol propoxy sulfates, internal olefin sulfonates, and branched alpha olefin sulfonates were identified as good EOR surfactants using this screening process. These surfactants are available at low cost and are compatible with both polymers and alkali such as sodium carbonate and thus are good candidates for both surfactant-polymer and alkali-surfactant-polymer EOR processes. One of the best formulations was tested in both sandstone and dolomite cores and was found to give excellent oil recovery and low surfactant retention.

Several high performance, low-cost surfactants for EOR were identified and tested starting with an efficient laboratory screening process that emphasized observations of phase behavior and viscosity. This screening process had been shown to provide reliable selection of cost effective surfactants, co-surfactants and polymers as a function of salinity, hardness, alkali, temperature, and rock type. Surfactant structures with branched hydrophobes were found to be the most suitable for EOR because

microemulsions made from these surfactants show small tendency to form viscous phases such as gels and liquid crystals that result in high surfactant retention. Adding propylene oxide to the surfactant improved its performance with small increase in the cost which is a very practical approach towards changing the surfactant to the specific crude oil and reservoir conditions. The surfactants investigated gave high oil recoveries and low residual oil saturations (S_{oil} = 0.03) in both sandstone and carbonate reservoirs flooded under low pressure gradients of typical values in oil reservoirs. These surfactants also showed low retention in both sandstone (0.08 mg/g) and in the carbonate reservoir rock (0.24 mg/g). The low surfactant retention was attributed in part to low viscosity microemulsions that were selected using the qualitative phase behavior testing described in this study. Sodium carbonate was observed to speed up coalescence to equilibrium microemulsions and was also expected to decrease surfactant adsorption on both sandstone and carbonate rocks, so its use in some applications should provide additional benefits.

Wu & Shuler (2005) investigated one class of anionic surfactants, a series of branched alcohol propoxylate sulfate surfactants, as candidates for chemical EOR applications. The experimental results showed that these surfactants may be the preferred candidates for EOR as they can create low interfacial tension (IFT) at dilute concentrations without requiring an alkaline agent. Also, some of the formulations exhibited a low IFT at several percent sodium chloride concentrations, and hence might be suitable for use in reservoirs of higher salinity. Adsorption tests onto kaolinite clay indicated that the loss of these surfactants was comparable to or in some cases greater than the other types of anionic surfactants. Surfactant performance was evaluated in oil

recovery core flooding tests. Selected formulations displaced most of the water floods residual oil in place even with dilute, 0.2 wt% surfactant solutions from sandstone cores.

The anionic surfactants investigated in this research were branched alcohol propoxylate sulfates, sodium salt, manufactured by Sasol North America Inc. The trade names of these commercial anionic surfactants are Alforterra mn. In the nomenclature Alfoterra mn, the second digit n (e.g., 5 in Alfoterra 15) indicates the average number of propoxy groups in the molecule. The first number (m) is associated mainly with size of the branched alkyl chain. Alfoterra 1n, 2n, 3n, 4n, 5n, and 6n series have an alkyl chain of approximately C13, C12,C14, C12-C13, C14-C15, and C12-C13, respectively. An example of molecular structure is shown in Figure 2-2.

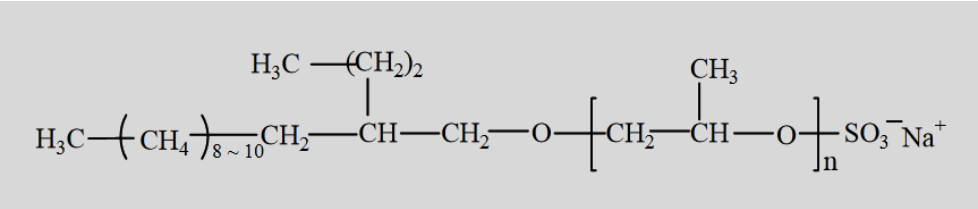


Figure 2-2 Branched Alcohol Propoxylate Sulfate, Sodium Salt (Wu & Shuler, 2005

Major results observed from this study showed that branched alcohol propoxylate sulfate surfactants at concentrations as low as 0.1 wt % created an IFT of 0.01 mN/m, or even less, between a brine and a crude oil. The optimal salinity (minimum IFT condition) was several percent NaCl for the products tested. The optimal salinity decreased with an increase of propoxy groups. Generally, adsorption of these surfactants on kaolinite clay decreased with an increase of the number of propoxy groups. The amount adsorbed was in the range of 3 - 25 mg per gram kaolinite at equilibrium concentrations of 0.4% wt or lower; and 4 - 65 mg per gram clay at around 2 % wt concentration.

The alkali in alkaline-surfactant-polymer (ASP) flooding usually causes problems of scaling and emulsification, the surfactant-polymer (SP) flooding was proposed for enhancing heavy oil recovery in China. It was observed that in the past to reduce the interfacial tension (IFT) to an ultra-low value, alkalis were used. Feng & Zhang in 2012 presented a type of betaine surfactant which showed an excellent ability to reduce oil/water IFT at low concentration without alkali, and alkali lignin with low-price was compounded as a sacrificial agent to reduce the adsorption. They conducted sandpack flooding tests to examine the effectiveness of enhanced oil recovery by compound chemical system containing polymer, betaine and alkali lignin.

Four types of betaine surfactants were tested by the indictor of oil/water dynamic IFT, and SBET-12 was selected as the surfactant to be used in compound flooding because it reduced the IFT to an ultra-low value over a wide concentration range. The adsorption of SBET-12 decreased significantly by approximately 40% when low-cost alkali lignin was added, resulting in a minimal adsorption value of only 1.078 mg/g. The primary mechanism for this decrease in the adsorption capacity was the reduction in the

electrostatic attraction between quartz sand and the betaine surfactant molecules as the compound system became weakly alkaline with the addition of alkali lignin. The results of the dynamic IFT and the rheology tests demonstrated that the added HPAM and alkali lignin did not have a significant effect in reducing oil/water IFT. Sandpack flooding tests were conducted for different systems, the results showed that SBET-12, alkali lignin and HPAM had good synergy with each other in compound flooding, producing the maximum tertiary recovery up to 20%.

2.3 Wetability Alterations

Gaurav Sharma et al. (2011) worked on changing the wettability of a carbonate rock at high temperature and high salinity from mixed wet to a water wet. Three types of surfactants were used screened on the basis of different experiments initially performed. First screening was done on the basis of aqueous stability in harsh conditions. Then aged calcite plates were used to perform contact angle experiments and in the last spontaneous imbibition were conducted on field cores for some surfactants which showed promising behavior in previous experiments. Some surfactants were not stable in aqueous stability experiments. Dual surfactants, which are the mixture of cationic and non-ionic surfactants, increased the stability and some of them were very good in changing wettability.

Initially cationic surfactants with 0.2% were used in the solutions and IFT was measured for each one of them and then dual surfactants were used with different combinations and cloud points and IFTs were measured for each sample. As most of the non-ionic surfactants were found to be unstable in aqueous solutions, they worked when used with the cationic surfactants. With the addition of the surfactant, the IFT definitely

decreased. This work also showed that without surfactant when oil is dropped on the calcite plates, it sticks to the plate and shows oil wet behavior but when the surfactant is added to the solution, its behavior changes and oil moves on the surface while water starts getting stuck on the surface. So this was the main purpose of adding the surfactant in the solution to change the wettability and mainly it was measured using the contact angle. The solution containing these surfactants was named as modified water and a comparison was drawn between the simple water flooding and modified water flooding experiments.

. The main results obtained by the experimentation are as follows:

- Water wetness of calcite plate decreased as ethoxylated groups of non – ionic surfactants was increased.
- Dual surfactants worked better in high salinity and high temperature conditions due to aqueous stability.
- Dual surfactants containing cationic and non-ionic surfactants were able to recover more than 70% if used in dilute concentrations.
- From the core flood experiments it was observed that modified water flooding increased the oil recovery at lab scale from 29 to 40%.

A. Seethepalli et al. (2004) studied wettability alteration for surfactant flooding in carbonate reservoirs. In this work, ten surfactants were tested. Surfactants 4-22, 5-166 and S-6566 were alkyl aryl sulphonates. Alfoterra series are alkyl propoxylated sulfates from Sasol. DTAB is dodecyl trimethyl ammonium bromide which is a cationic surfactant used as a reference. He observed the interactions of dilute alkaline anionic

surfactant solutions with crude oil. Several experiments were conducted including wettability, phase behavior, interfacial tension and adsorption. In phase behavior study, dilute solutions of surfactant were prepared with different concentrations of sodium carbonate. In interfacial tension study, IFT was measured with the use of spinning drop tensiometer. In wettability test, contact angle measurements were performed with the help of a Kruss goniometer. It was observed that anionic surfactants (SS-6656, Alfoterra 35, 38, 63, 65, 68) had the potential for changing the wettability to intermediate water-wet with performance better than the cationic surfactant DTAB. Also, carbonate surfaces showed similar wettability behavior with surfactant 4-22. Anionic surfactants (5-166, Alfoterra-33, Alfoterra-38, Alfoterra-68) reduced the interfacial tension with a West Texas crude oil to low values.

Gupta et al (2008) studied the effect of salinity, surfactant concentration and temperature on the wettability alteration. Contact angles, phase behavior, and interfacial tensions were measured. They concluded that there exists an optimal surfactant concentration for different salinity and an optimal salinity for different surfactant concentration at which the wettability alteration was maximum for the anionic surfactants. With increasing reservoir salinity, the extent of maximum wettability alteration decreased for a surfactant, but the surfactant concentration needed for the maximum wettability alteration decreased. IFT and contact angle were found to have the same optimal salinity for a given concentration of anionic surfactants. As the number of ethoxylate groups increased in anionic surfactants, the extent of wettability alteration also increased. Wettability of carbonates can be altered by divalent ions at high temperature (90°C and above). Sulfate and calcium ions played a more important role in altering

wettability than magnesium ions. Wettability alteration increased the oil recovery rate from fractured carbonates.

2.4: Core Flooding

In cEOR many chemicals were analyzed on a lab scale experiments and were screened out to be used in the real field. Major issue faced in past was chemicals performing best on a lab scale were not able to expected results in field. But still there were no other ways to test the chemicals and recommend the best one for field tests. Previous techniques used were to define the properties of chemicals and these techniques give an idea that these surfactants can perform better like IFT was used for screening of surfactants but when we studied the literature it was concluded that IFT was not always correct in recommending surfactant. Surfactants are added in solution to reduce the IFT between brine and oil, and the surfactants which gave ultra-low IFT were presumed to be the best for cEOR. But Yefei Wang (2010) during his work on non-ionic surfactants concluded that this statement was not always correct. Non-ionic surfactants were not always expected to perform best in the field and oil recovery tests. Core flooding experiments were used to analyze which surfactant and polymers are giving better oil recovery. Core flooding experiments actually are the pilot plants which represents a sketch of real reservoirs and conditions are kept nearly equal to real reservoirs to check the performance of different experiments. As in our work we used non-ionic surfactant and alcohol propoxylate surfactants , literature was consulted about the performance of similar surfactants. Wang et al (2010) used cocamide DEA, a non-ionic surfactant to study its performance during IFT and core flooding in comparison with the petroleum sulfonate , an ionic surfactant and concluded that IFT was not always able to screen the

best surfactant. During IFT experiments, DEA was not able to give ultra-low IFT values but PS was producing ultra-low IFT values. But when these surfactants were used in core flooding along with polymer they produced opposite results. PS with ultra-low IFT values was able to produce 23% oil during core flooding tests but surfactant giving low IFT values were able to produce oil up to 34% and that was big difference if surfactant was to be selected on core flooding tests, surfactants with low IFT values will be preferred than surfactant giving ultra-low IFT values. With this it was suggested that core flooding tests give much better recommendations for suggesting chemicals for cEOR than IFT and other techniques.

Second class of surfactant we used was from the propoxylate family containing propoxy groups. A lot of work has been done in the past on this class if surfactant when it comes to core flooding and IFT. Alcohol propoxylate sulfates (APS) surfactants were famous for being tolerant to high salinity conditions and Internal Olefins Sulfonates (IOS) were known for being stable at high temperatures. Flaaten et al (2008) worked on the combination of these surfactants and performed preliminary tests of phase behavior and IFT to find out the best combination that could produce maximum oil during core flooding. After trying different combinations, the best combination was APS and IOS with same concentration and without any co-solvent in combination with the polymer. Core flood experiment was performed in two steps, in first slug, surfactants and polymers were used, in the second slug only polymer was used with some electrolyte and overall oil recovery was increased up to 95% with the combination of these two. APS and IOS when combined performed best as APS was able to tolerate the salinity and IOS made the solution stable even in the presence of APS but at higher temperature. Alkalis were also

being used in combination with surfactants; these surfactants could reduce the cost of surfactants and were able to give oil recovery up to 96%. Alkalis were consumed before surfactants and reduce the overall salinity of the solution and converts hard water to soft water and this increase the performance of the surfactants during the recovery. Surfactant, Surfactant-Polymer and Surfactant-Polymer-Alkali (ASP) flooding all three types of flooding were turned out to be best for particular conditions and all three chemicals had roles in recovering oil. In many fields cEOR had been applied and results obtained were positive but still a lot of work is needed in developing more combinations and modifications for particular chemicals.

Chapter 3

METHODOLOGY

3.1 Materials

Two main materials were used in this project, Polymer and Surfactants. The main purpose of this project was to study the behavior of surfactants when used in combination with the polymers for cEOR.

3.1.1 Polymer:

In this work, hydrolyzed polyacrylamide HPAM (FLOPAAM) was used supplied from SNF FLOERGER in France (http://www.snf-group.com/-English-.html). This polymer has different grades. It is stable up to the temperature of 90^{o}C and has a molecular weight of 13 million Dalton with 25-30 mole% hydrolyses. The polymer concentration was kept constant at a value of 0.25 g/100ml solution. Structure of HPAM is shown in Figure 3-1.

3.1.2 Surfactant:

Two Surfactants were used in this study. First surfactant was Marlipal O13. The products of the MARLIPAL® O13 series from Sasol are alkylpolyethylene glycol ethers and they belong to the class of nonionic surfactants. Isotridecanol, a C13-oxo alcohol prepared from a C12-olefin mixture, is a synthetic alcohol on which these products are based. Three grades of Marlipal were used and these were Marlipal O13 (79, 99 & 120) Marlipal O13/79 and Marlipal O13/99 were 90% pure and remaining 10% was water whereas Marlipal O13/120 was 100% pure and was in the gel form. Marlipal in non-ionic surfactant and its CMC value was around 0.01%. Alfoterra 123-8s is an anionic surfactant and is also known as alcohol propoxylate sulfate. 8s represents the number of propoxy groups present in each molecule and it has 8 propoxy groups. This surfactant was 88% pure containing 7.7% free water and rest was Unsolphated matter. It contains sulfate

group at the end of chain and these surfactants are known to be thermally stable only at room temperature. Important properties of Marlipal O13/120 and Alfoterra 123-8s are listed in Table 3-1. Structure for both Alfoterra and Marlipal are shown in Figure 3-2.

3.1.3 Brine:

Brine solution was used for all experiments to investigate the effect of salinity. In most of the experiments salinity was 57000 ppm nearly equal to actual sea water salinity. Composition of this brine is shown in Table 3-2.

3.1.4 Crude Oil:

Oil used for adsorption, phase behavior, IFT and core flooding was adopted from Uthmaniyah Oil Field, Saudi Arabia. It is light crude oil with API gravity of 30. The density of crude oil was 0.8757 g/cm^3 with molecular weight of 251 g/mol and viscosity of 13.1 cP. Composition of oil is given in Table 3-3.

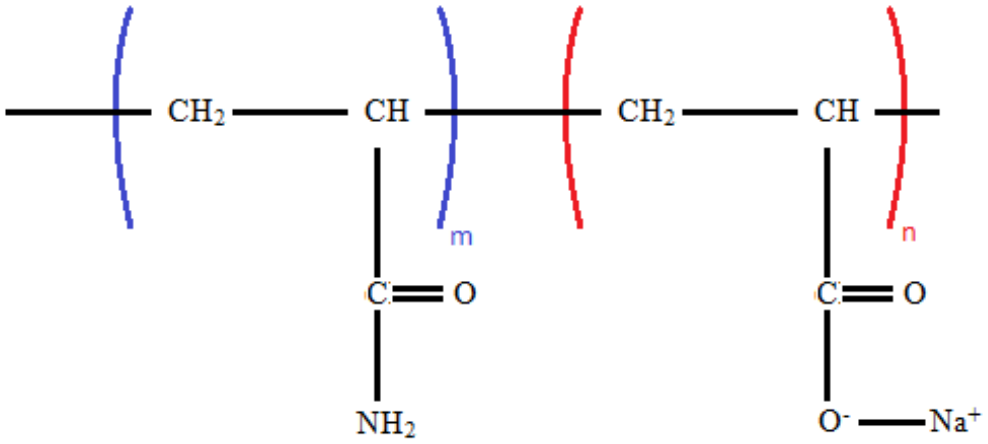
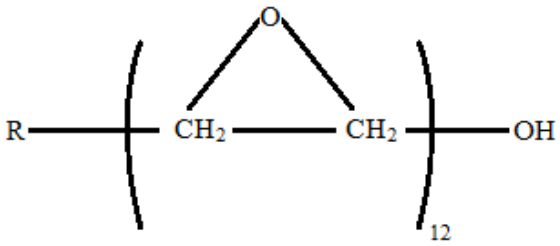
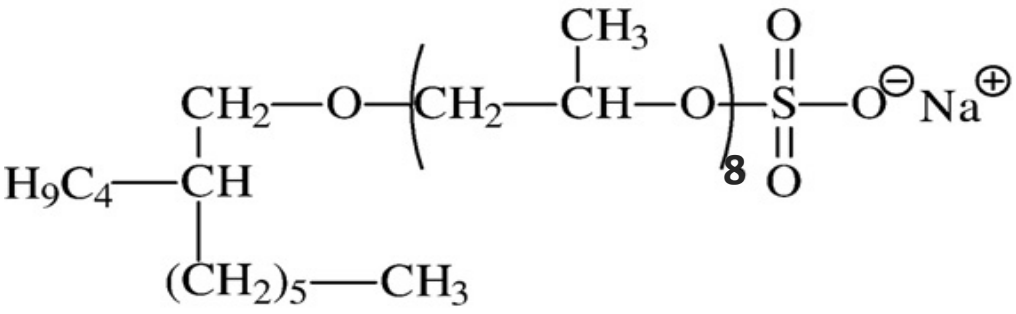


Figure 3-1 Structure of HPAM (FLOPAAM 2530s)



(a)



(b)

Figure 3-2 (a) Marlipal O13/120 (b) Alfoterra 123 – 8s

Table 3-1 Properties of surfactants

Surfactant	**Marlipal O13/120**	**Alfoterra 123-8s**
State	Gel/Liquid	Liquid
Color	White	Brown
pH	5-7	ca. 9
Density	ca. 1g/cm^3	ca. 1g/cm^3
Viscosity	ca. 40 mPa.s	-
Flash Point	>180 ^oC	>101 ^oC
Composition	100 % pure	88% Active components 6% water 6% Unsolphated Matter
Water Solubility	Completely miscible	Completely miscible

Table 3-2 Brine Composition

Salt	Concentration (g/L)
$NaHCO_3$	0.1652
Na_2SO_4	6.3390
NaCl	41.1724
$CaCl_2$	1.8021
$MgCl_2$	8.1595
Total salinity (TDS)	57.64

Table 3-3 Crude Oil Composition

Component	Moles	Mole %
C5	0.00216	1.23
C6	0.007434	4.23
C7	0.018767	10.67
C8	0.027806	15.81
C9	0.025519	14.51
C10	0.025371	14.43
C11	0.019607	11.15
C12+	0.049211	27.98
TOTAL	0.175876	100

3.2 Experimental Procedure

Experimental procedure was followed as shown in Figure 3-3. Samples were prepared at first stage. Rheology tests were performed for analysis of the SP systems. After that surfactants were analyzed through thermal stability, phase behavior, adsorption and interfacial tension tests. Best formulations were used at the end in core flooding experiments

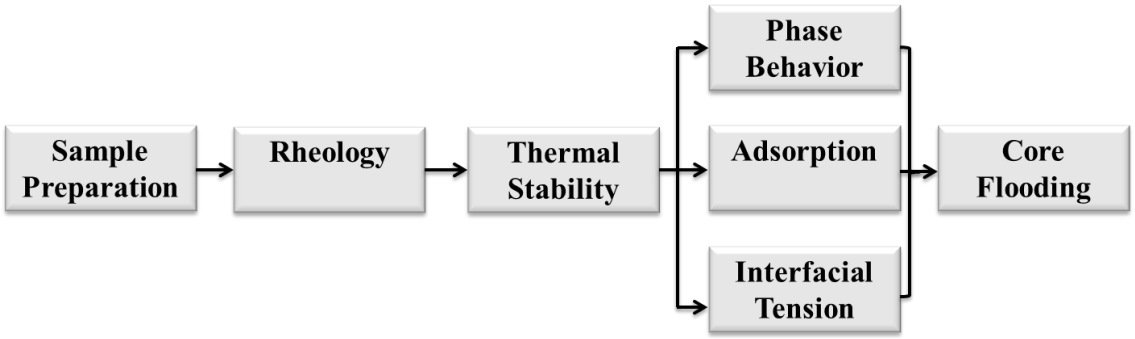


Figure 3-3 Flow chart for experimental procedure

3.3 EXPERIMENTATION

Samples of different compositions and salinity were prepared. First samples were tested for thermal stability against different temperatures and for different time limits. Those samples which passed the thermal stability tests were further characterized for rheology. Different rheological tests were carried out to cross check the thermal stability and compatibility of the surfactant and polymer systems. Different properties were determined using these tests and factors like salinity, temperature, composition which affects solution properties were sorted out as the dominant factors. Structure of the solution samples was studied using NMR/FTIR. These samples were then exposed to aging for different temperatures and times to ensure the stability of the solution. Major

structural changes were studied using NMR. After thermal stability, surfactants were characterized using phase behavior, adsorption and IFT experiments and optimum concentration of surfactants was found and this concentration was used for core flooding experiments.

3.4: SETUPS AND EQUIPMENT

The experimental setups used in this work are mainly:

- Rheometer
- FTIR
- NMR
- Phase Behavior apparatus
- Adsorption apparatus
- Flooding apparatus

3.4.1: RHEOMETER (RHEOLOGY):

Rheometer used for rheological studies was from TA named as Discovery Hybrid Rheometer (DHR). It was used for rheology as well as for thermal stability tests as it can cover a wide range of temperatures. It consists of several geometries but we considered only one of them, namely:

- **Concentric Cylinders** (Without Pressure)

This geometry consists of a jacket, inner cylinder (cup) with diameter of 30.39 mm and a rotor (bob) with diameter of 27.97 mm and length of 41.90 mm. Both cup and bob are made from Aluminum. 22.4 ml of sample was required for each run. Temperature was controlled using heating through peltier element and circulating water cooler. In Figure 3-4 complete geometry of concentric cylinder setup is shown. The following tests were also carried out:

- **Flow Sweep**: In this test, temperature remains constant and viscosity was measured against shear rate. Shear rate increases constantly with time and its range was between 10^{-3} – 10^{3} s^{-1}. From this test, behavior of the sample was observed e.g. how much viscosity decreases as the shear rate was increased. Two temperatures were used for this test, low temperature 50 ^{o}C and high temperature 90 ^{o}C.
- **Temperature Ramp**: This test was opposite to flow sweep, as shear rate was fixed at 1 s^{-1} and temperature was increased with time and viscosity was measured against time. This test was used to cross check the thermal stability as measured by FTIR/NMR. Temperature range was fixed between 30 to 90 ^{o}C.
- **Frequency Sweep (Oscillation)**: Temperature and strain rate was fixed in this test and frequency range was set between 0.01 – 100 s^{-1}.This test was used to find out the storage and loss modulus and the investigate viscoelastic properties of samples.

Polymer solution Preparation:

Surfactant and polymer solution preparation need extra care during preparation. Solution was prepared in a sequence of adding surfactant in distilled water following with the polymer although sequence has no major effect on the solution but this sequence was followed to make sure that it has no effect on any of the measured property. The solution was prepared by adding the required concentration of surfactant in distilled water while stirring was continued at a nominal speed as surfactants were in liquid form. Then speed was increased to 300 rpm and polymer in a powder form was added at the rim of the vortex very slowly to avoid formation of clogs or agglomerates, after addition of polymer speed was reduced to 120 rpm and kept at the same rate for 24 hours. All solutions were prepared in the same procedure.

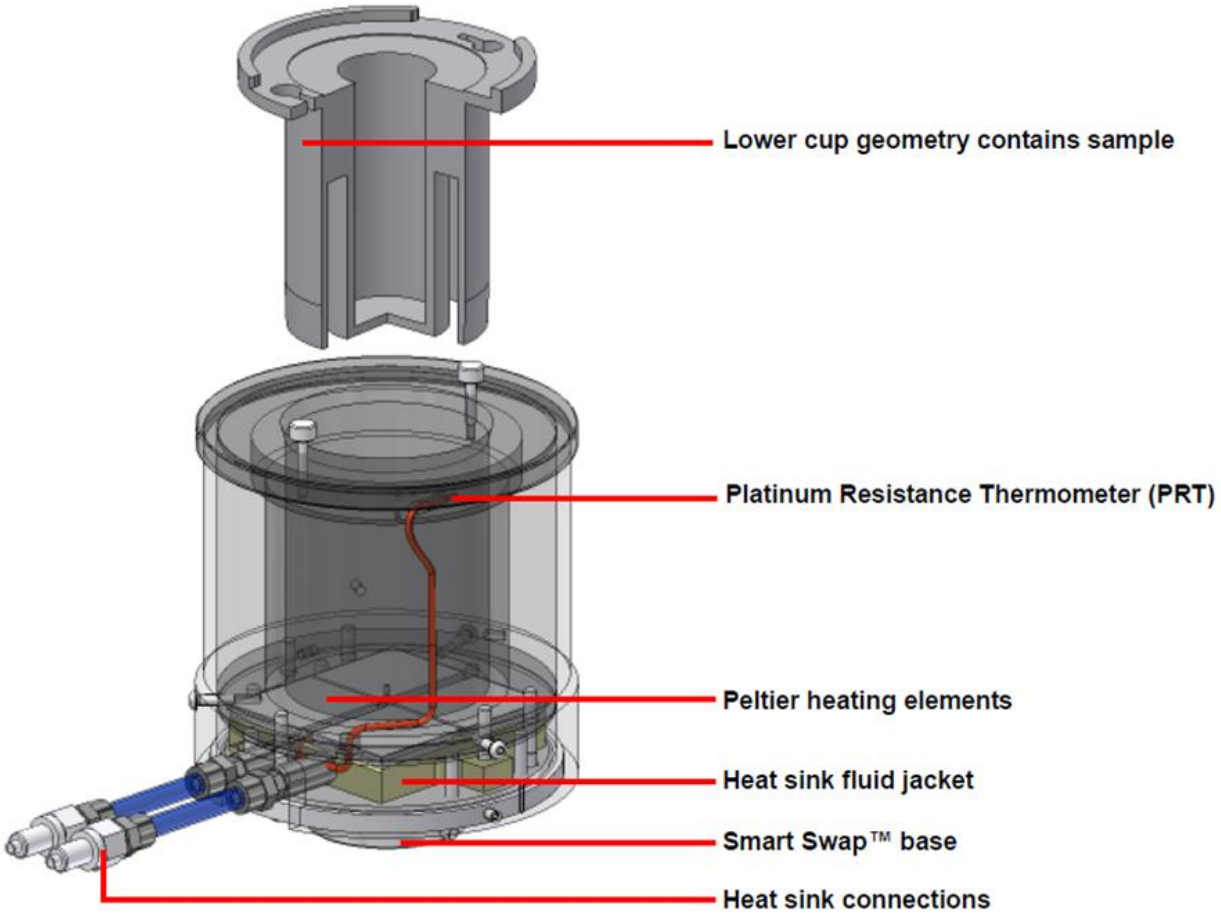


Figure 3-4 Concentric Cylinder geometry of DHR Rheometer

3.4.2: Thermal Stability Tests:

Thermal stability of pure surfactants was studied in two stages. In first stage samples was tested using Thermo Gravimetric Analysis (TGA) - TA Instruments SDT-Q600 TGA. TGA measured the weight of the sample placed in an aluminum holder and temperature was increased at a constant rate from 20 ^{o}C to 1000 ^{o}C. Samples started degrading and evaporating after certain temperature and it was indicated by the weight loss. In TGA results, weight percent is plotted against temperature to get idea at what temperature surfactant started degrading. In TGA samples were exposed to severe conditions but at a very high rate of 10^{o}C/min.

In a second stage samples were aged for different time periods and structural changes were analyzed using Fourier Transform Infrared Spectroscopy (FTIR) and Nuclear Magnetic Resonance (NMR). Both surfactants were pure in liquid form so for all experiments they were used directly. Aging was done at 80 ^{o}C in oven. Samples were placed in small vials with cap and weight was measured before and after aging to avoid any weight loss during aging. FTIR (Thermo Scientific Nicolet 6700 FT-IR) uses infrared spectra to explain structural changes in the sample. Every functional group has unique wavelength value FTIR compare the spectrum of samples before and after aging. Those samples that were not thermally stable produced different spectra after aging. For detailed explanation of thermal instability of surfactants NMR was used. NMR-Proton and NMR-Carbon experiments were performed to find the number of functional groups containing carbon before and after aging. Comparing spectra for samples before and after aging explained what structural changes occurred during aging.

3.4.3: Static Adsorption Tests:

Adsorption of surfactant, cations and anions on the rock surface plays an important role in screening out chemicals for cEOR. Chemicals are expensive and if surfactant is lost during adsorption then these surfactants are screened out for economic reasons. Static adsorption tests were performed to study how much surfactant gets adsorbed. Precipitated Calcium Carbonate (PCC) powder was used to represent carbonate reservoir and in the power form it has higher surface area so that if surfactant shows little adsorption on this it will perform much better on real carbonate rocks. Two parameters were studied in these tests; temperature and presence of oil. Temperatures used were 25^{o}C and 90^{o}C. Experimental procedure was as follows:

- In 40ml vial, 2 grams of PCC were added
- 30 ml of sample solution with fixed concentration of surfactant was then added
- Vials were then capped and sealed to avoid any losses were put into water bath shaker for 24 hours.
- Samples were then left to equilibrate at constant temperature for next 24 hours.
- Water bath shaker was used to maintain the temperature during the whole experiment.
- After equilibration, samples were taken out, filtered through 0.45 µm pore diameter filter paper. Samples were then analyzed by Ion Chromatography (IC) for cations and anions and by UV-VIS for surfactant concentration. Samples before adsorption were used as reference.
- Ions adsorption and surfactant adsorption results were used to calculate adsorption density for each ion and surfactant using following equation:

$$\Gamma = \frac{(C_i - C)V}{M} \qquad (3.1)$$

'Ci' is the initial concentration (ppm); 'C' is concentration after adsorption (ppm); 'V' is volume of sample (l) and 'M' is weigh of adsorbent (PCC) (g).

3.4.4 Phase Behavior Experiments:

Phase behavior experiments are usually performed to screen out surfactants to find which one will be able to give ultra-low IFT. When surfactant solution and oil are mixed it will produce one of the three types of Winsor Type micro-emulsions. Winsor (1954) defined the micro-emulsions as Type I, Type II and Type III. Type I is oil in water micro-emulsion in which oil molecules are surrounded water and surfactant molecules. Type II is water in oil micro-emulsion and in this water molecules are surrounded with oil molecules. Type III is the mixed phase micro-emulsion or middle phase micro-emulsion and it is preferred for cEOR as it represents the best interaction of surfactant with oil. As salinity is increased, surfactants solutions micro-emulsions change from Type I to Type III and then Type II. Phase behavior experiments were performed to find optimal salinity for each surfactant. Optimal salinity is the salinity at which oil and water solubilzation ratios are equal $\sigma_o=\sigma_w$. Water solubilization 'σ_w' ratio is defined as Volume of water in microemulsion V_w per volume of surfactant V_s and0. oil solubilization ratio 'σ_o' is defines as volume of oil in micro-emulsion V_o per volume of surfactant V_s. At optimal salinity solution gives ultra-low IFT values. IFT could be measured through phase behavior experiments and but we measured IFT with conventional methods. It was done just to see the interaction between surfactant solution and oil and which type of micro-emulsions will be produced. Experiment was divided into two sets for each sample. In first set, concentration of surfactant was varied and salinity was fixed at 1M NaOH to find optimum concentration where Type III micro-emulsion is formed. Six samples were

prepared in first set with six different concentrations of surfactants that were 0%, 0.1%, 0.2%, 0.3% 0.4% and 0.5% for both surfactant systems. Salinity scan test performed by fixing optimum concentration of surfactant concluded from first set. Salinity was varied from 0k, 10k, 20k, 30k, 40k and 50k ppm. Tests were performed at two temperatures to check the stability of surfactant solution at higher temperature and study the surfactant performance at severe conditions. The experimental procedure was as followed:

- Surfactant solution was prepared with defined salinity in DIW
- 5ml of solution was put in 15ml graduated glass tube
- 5ml of oil was then put at the top as it is lighter phase. Total volume of sample was 10ml and initial interface was at 5ml
- Tubes were caped and sealed to avoid any leakage and then they were rotated at 30rpm for 24 hours to get good mixing of the samples. This was done at room temperature.
- Tubes were then placed vertically straight to achieve equilibrium
- Images were taken at regular intervals to monitor the micro-emulsions.
- Same procedure was repeated for higher temperature, rotation was done inside oven and tubes were kept in oven for equilibrium.

3.4.5: Interfacial Tension Study:

IFT was measured using SITE 100 Spinning Drop Tensiometer shown in Figure 3-5. IFT was measured between light phase (oil) and heavy phase (surfactant solution). This instrument was capable of measuring ultra-low IFT up to 10^{-6} mN/m but was not feasible for higher IFT values as upper limit was restricted up to 20 mN/m. A capillary made of glass was used where light and heavy phase come into contact. The capillary was initially

filled with heavy phase, drop of light phase was introduced and shape and dimension of droplet was used to measure the interfacial tension between two phases. The droplet rotates when capillary was rotated with particular angular frequency and axis of rotation of droplet and capillary were parallel. The radius of droplet reduces with high angular frequency due to centrifugal forces. The radius of droplet depends on IFT (γ) betweem two phases, angular frequency (ω) and density difference between two phases (ρ_H-ρ_L). IFT (γ) was then calculated using Bernhard Vonnegut equation:

$$\boldsymbol{\gamma = \frac{1}{4}(\rho_H - \rho_L)\omega^2 R^3} \qquad (3.2)$$

Where, ρ_H and ρ_L are densities (kg/m^3) of heavy and light phase respectively, ω is the angular frequency (1/s) and R is the radius of the droplet (m). Capillary diagram is shown in Figure 3-6. Parameters studies were surfactant concentration, salinity, temperature and effect of co-surfactant on the IFT. The experimental procedure was followed as:

- The oil circulation system was used to control the temperature of the system and it was turned from the beginning to stabilize the required temperature.
- The capillary was filled with heavy phase (surfactant solution)
- Air bubbles and other impurities (if any) were removed and capillary was cleared and filled only with heavy phase
- A Calibration wire was used to define scale factor for each sample.
- Illumination and magnification was adjusted during calibration and fixed
- Information was entered about both phases in the software to calculate IFT
- Rotation was set at around 1000 rpm and light phase (oil) was injected using a syringe

- A camera was used to take images for every instant. There was an option to set sequence of taking images or we can do it manually. IFT was calculated based on the image captured
- Rotation was then adjusted to stabilize the droplet and level of capillary was also adjusted to keep droplet in view of camera
- The temperature was then maintained using oil circulation bath and varied for particular experiments.

Figure 3-5 SITE 100 Spinning Drop Tensiometer

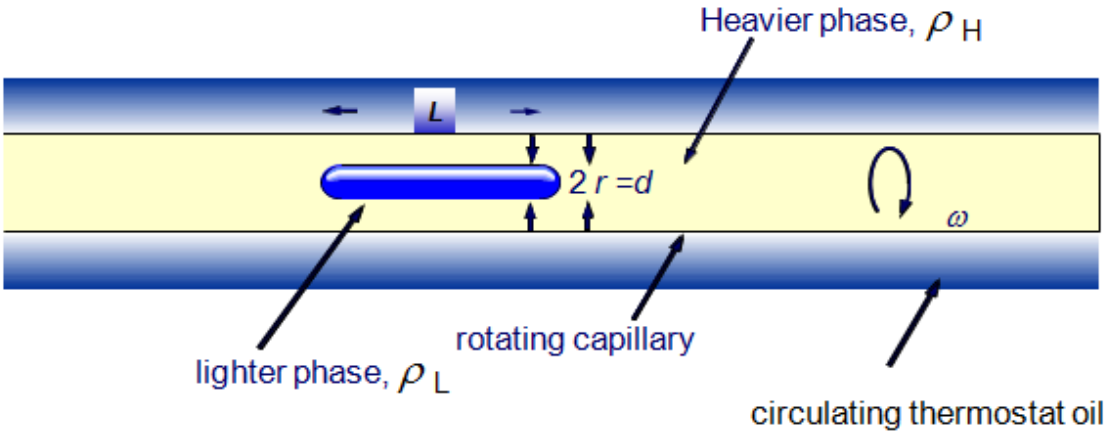


Figure 3-6 Capillary Diagram of Tensiometer

3.4.6: Core Flooding:

At the end, samples with best formulation were used for core flooding experiments in which dynamic adsorption and oil recovery was measured and studied continuously at the reservoirs conditions. Indiana Limestone core was used as a sample from carbonate reservoir and approximate conditions of the reservoir were applied to sketch the same picture of reservoir in the field. Core samples used were 12 in long and 1.5 in of diameter. Two core samples were used for two systems in our case. Pore Volume was calculated for each core and found to be 56 and 65 cc. Permeability was calculated using formation water and was in the range of 70 to 80 mD. Oil recovery was measured for three steps as we injected brine, surfactant-polymer solution (SP Solution) and then brine was injected at the end. The composition of the solutions was finalized from the previous rheology and IFT analysis. The equipment used was FDES-645 USA for core flooding. In this setup sample up to 12 inch long can be treated. Four accumulators were in line with the core holder and four solutions of brine, formation water, SP-solution and oil were transferred into these accumulators. It has the auto building confining pressure system and Quizex pump system to flow liquids through the core with back pressure assembly to create pore volume up to 5000 psi. Core holder was placed inside the oven and temperature of oven and core was monitored continuously. Core flooding experimental procedure was followed as:

- The cores were cleaned using toluene at 80^{o}C temperatures to evaporate toluene from the core and other impurities were removed in the core cleaner. Then core was dried at 75^{o}C
- Vacuum was applied to remove air from the core for more than four hours.

- The core was then flooded with formation water to saturate it. Dry weight was measured before saturating with formation water. Salinity of formation water was 213734 ppm and saturation was done at 2000 psi confining pressure and saturation was continued for one day. After saturation, the wet weight was measured and the core was immersed in formation water for ions equilibrium.
- Pore volume was calculated as:

$$Pore\ Volume\ (PV) = \frac{Wet\ Weight - Dry\ Weight}{Density\ of\ Formation\ water} \qquad (3.3)$$

- The core flooding system was then made ready for the experiment. All precautions were taken to avoid any troubleshooting during experiment.
- The core was placed inside a core holder with suitable spacers inside rubber sleeve.
- The confining pressure was built as the first step up to 1000 psi and leaks were checked. When there was no leakage and system was set to perform, all connections were made.
- Formation water was injected in upstream and downstream piping and flushing was done to remove any air in the lines. Back pressure was also applied of 500 psi.
- The permeability was calculated when formation water was injected at four different flow rates of 0.25, 0.5, 0.75 and 1 cc/min with 500 psi pore pressure and stabilized pressure drop was measured for each flow rate. Darcy law for linear flow through porous medium was used which to calculate the permeability:

$$Permeability\ (K) = \frac{245\ Q\ \mu\ L}{A\ \Delta P} \qquad (3.4)$$

Where K is in mD, Q is flow rate (cc/min), L is length of core (cm), A is the cross sectional area of core sample (cm^2), μ is viscosity of formation water (cP) and ΔP is the pressure drop (psi) across the core. Figure 3-7 shows core flood system.

- After saturation the core was ready for flooding with SP solution. All solutions were placed in accumulators and temperature was maintained at 90^oC using oven.
- Core was first saturated with oil. This system had the facility to flow the solution forward and backward and direction could be change. Oil was injected at flow rate 5cc/min. Formation water produced was measured to calculate how much initial water saturation was reduced. The initial oil saturation (S_{wi}) was 100% as the core was saturated with formation water. After flooding with oil, S_{wi} was calculated as:

$$S_{wi} = \frac{PV - formation\ water\ produced\ (cc)}{PV} \qquad (3.5)$$

- S_{wi} was reduced up to 35% for first core and 34% in second core. The core was flooded with oil at regular intervals for 15 days and aging was continued for 15 days.
- After aging oil recovery was started by injecting brine at 0.5cc/min. Oil produced was measured in 15ml graduated tubes for each 0.1 PV of brine injected. Brine used was of 57000 ppm salinity. Confining pressure was maintained at 2000 psi and back pressure applied was 550 psi. Pressure drop was monitored during whole experiment.
- After brine, SP solution was injected at 0.75cc/min and oil recovered was again measured using graduated tubes for each 0.1 PV of solution injected.
- SP solution made in sea water contained 0.25% HPAM and surfactant used were 0.3% Alfoterra in first core flood test and with same concentration of polymer Marlipal used was 0.1% and these concentrations were optimized after all previous tests performed. Solutions were made in 57000 ppm sea water.

Figure 3-7 Core Test FDES-645 USA (Core Flooding System)

Chapter 4

Results and Discussion

A series of experiments was performed and data was analyzed for each system independently. All results were combined to find out the effect of varying different parameters on different properties of the polymer-surfactant solutions. Major parameters varied during the experimentation were the temperature, concentration of the surfactant, salinity and effect of the co-surfactant. The surfactants used belong to the two different classes and the two systems were separated to investigate the effect of each parameter on each system independently.

4.1: Systems of Surfactants

The classification of the surfactants according to the structure and functional groups is as follows:

System – 1: Alcohol Propoxylate Sulfates (Alfoterra 123-8s)

+ Hydrolyzed Polyacrylamide (HPAM 2530s)

System – 2: Ethoxylated Sulfates (Marlipal O13/120)

+ Hydrolyzed Polyacrylamide (HPAM 2530s)

4.2: Experimental Techniques

A series of different experimental techniques were used to investigate the properties of each surfactant and the surfactant performance. Major techniques that were utilized included:

1. Rheology
2. Thermal Stability (TGA, FTIR, NMR)
3. Phase Behavior
4. Adsorption
5. IFT
6. Core Flooding

4.3: Rheology Experiments

Major experiments performed in the rheology study were flow sweep, frequency sweep and temperature ramp. Some of the experiments were performed to determine the initial parameters for the left over experiments, e.g., time sweep was performed to find out the optimum strain rate for the other experiments.

Three major factors were studied which could affect the performance of the surfactant in the field:

1. Concentration
2. Temperature
3. Salinity

Results for each system are discussed separately and the effect of each parameter is described in detail.

4.3.1: Effect of Concentration:

The polymer-surfactant solution was prepared as mentioned already in Chapter 3, section 3.4.1. First step was to observe the effect of the surfactant concentration on the solution rheology. Polymer concentration was kept fixed at 0.25 % for all the experiments and only the surfactant concentration affected the rheology. Major rheology experiments performed to investigate the effect of surfactant concentration were:

- Flow Sweep
- Frequency Sweep
- Temperature Ramp

Results for each experiment and for each system are explained below:

System – 1:

Marlipal O13/120 and HPAM:

From the past experiences and the data provided by the manufacturer of Marlipal surfactant, initial concentration was optimized to be used for rheology tests. In the literature it is stated that the surfactants were used to lower the interfacial tension (Garry Pope, 2007). But as the surfactant was introduced, it reduced the viscosity of the solution which further reduced the sweep efficiency. To minimize the effect of the surfactant, polymers were introduced to increase the viscosity of the solution which helped in increasing the sweep efficiency. To observe the effect of the surfactant concentration on

the viscosity of the solution, different solutions were prepared with concentrations of 0.05%, 0.1%, 0.15% and 0.2%.

Various experiments were performed to measure the viscosity of the solution, storage and loss moduli. To observe the effect of the concentration, temperature was first fixed at 50^{o}C and 90^{o}C. Before adding the surfactant, experiments were performed only for pure polymer as a reference.

Flow Sweep:

Concentric cylinder geometry was used to perform this test in which the only varying parameter was the shear rate and the measured parameter was the viscosity.

For the flow sweep experiment, temperature was fixed at 50^{o}C and the solution was prepared using De-Ionized Water (DIW). In this experiment, the range of the shear rate was within 10^{-2} - 10^{3} (1/s). Data was plotted as viscosity versus the shear rate and the shear rate was increased to see its effect on the viscosity with time. High range of the shear rate was covered to produce tough conditions that the solution will face during the flow in the reservoir.

First experiment was performed with the polymer only to set a baseline. The viscosity was measured against the shear rate at 50^{o}C. At low shear rate, the viscosity was higher by the order of three than the water viscosity. Structure of the polymer containing long chains was the main reason for the increase in the viscosity at low shear rate. The polymers are usually classified into two main categories; shear thinning and shear thickening. HPAM is a shear thinning polymer and it will show the decrease in the viscosity as the shear rate increases. When the polymer is mixed with water, polymer

molecules and cross linking across polymer molecules increases the viscosity of the solution. As the shear rate increases, crosslinks break due to the weaker bonds which result in decreasing the viscosity. In general, polymers are non-Newtonian fluids and the viscosity will not remain constant at higher shear rates. HPAM follows the shear thinning behavior and its viscosity decreases with the increase in the shear rate.

Behavior of the polymer viscosity is shown in Figure 4-1 in which the viscosity (Pa.s) is plotted against shear rate (1/s) in a log–log plot. The plot shows that at low shear rates, the polymer has a high viscosity compared to the water due to the high molecular weight structure of the polymer. At high shear rates, the viscosity starts decreasing until it is almost close to the viscosity of the solvent i.e., DIW. At the reservoir conditions, the viscosity of the solution was higher by the order of three than the viscosity of the water. The viscosity measured in this experiment was the absolute viscosity.

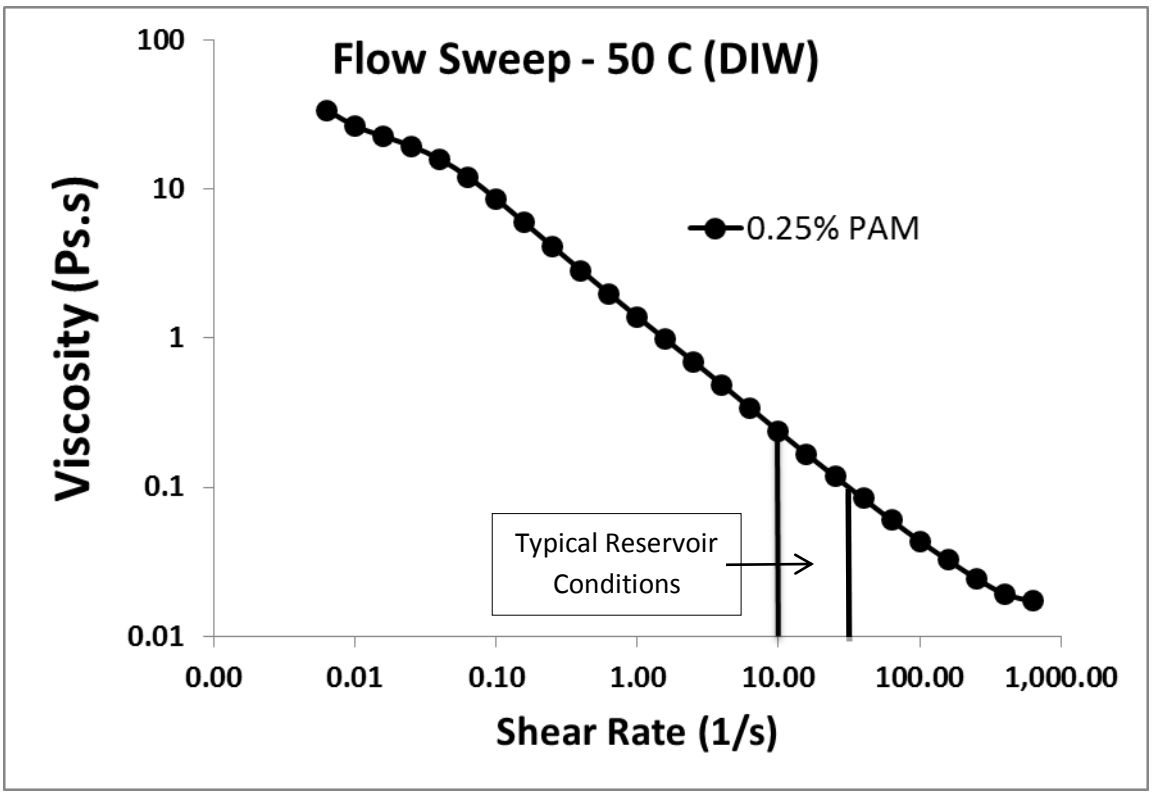


Figure 4-1 Effect of shear rate on the viscosity of HPAM Solution

The surfactants were used in small concentrations in EOR due to the high cost of the chemicals and thus an optimum amount of the surfactants was used. Polymer–Surfactant solution with varying surfactant concentration of 0.05%, 0.1% and 0.15% were prepared and polymer concentration was fixed at 0.25%.

Marlipal is a non-ionic surfactant so it does not interact with the molecules of the polymer both chemically and physically. No major decrease in the viscosity of the polymer solution was observed after the addition of the surfactant. Three different concentrations of the surfactants were used in the solution and the viscosity was measured for each solution. When plotted, it was observed that the viscosities were not following any particular sequence and were almost in the same range. Marlipal, being a non-ionic surfactant, did not participate in changing the bulk viscosity of the solution. Bataweel (2012) reported similar results for the surfactants where no change in the viscosity was observed. Plots were overlapping for all the three concentrations of the surfactant and the polymer. Effect of the surfactant concentration is shown in Figure 4-2.

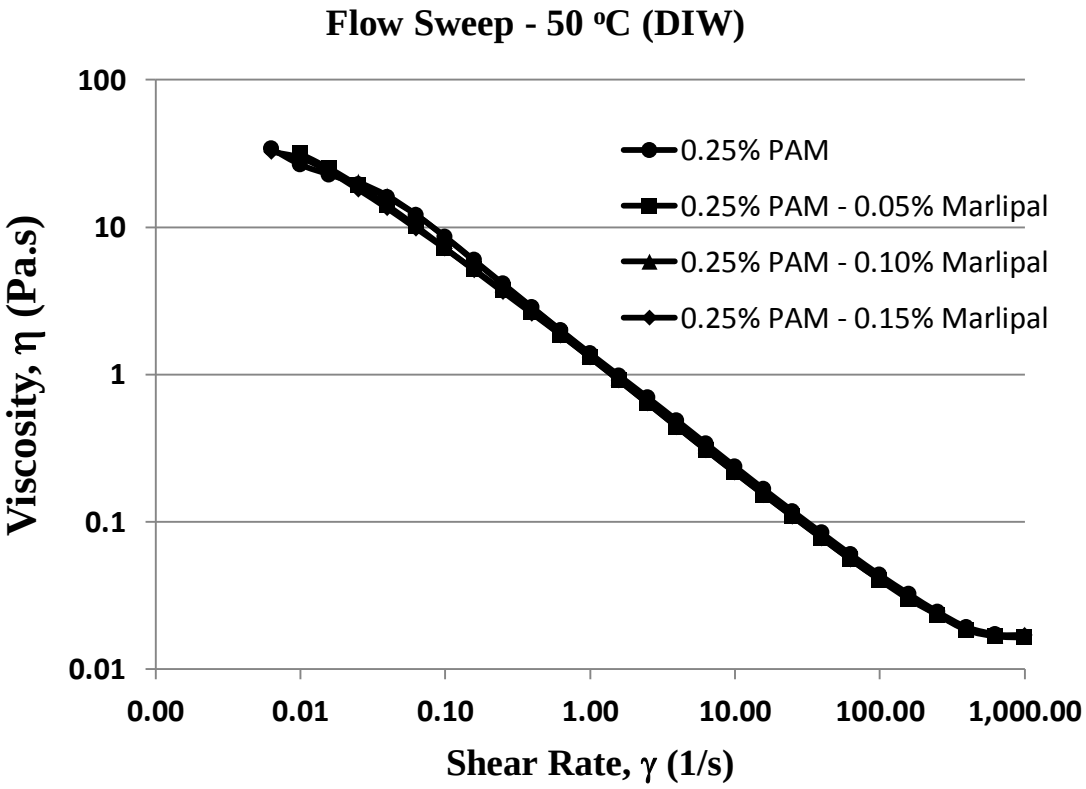


Figure 4-2 Viscosity vs shear rate for HPAM solution with different Marlipal O13/120 concentrations

Frequency Sweep:

The polymers are viscoelastic in nature and exhibit properties of both viscous liquids and elastic solids. Two very important moduli are used to investigate the nature of the polymers; Storage Modulus (G') and Loss Modulus (G"). Storage modulus is associated with the energy stored in the molecules and can be regained whereas loss modulus is associated with the energy lost and is usually referred to as viscous liquid. Storage modulus is associated with the elastic nature of any material.

In this experiment, storage and loss moduli were measured against the frequency. The strain rate was fixed for all the experiments at 25% and temperature was fixed again at 50^{o}C. This experiment was performed to observe what part in the polymer was dominating.

First experiment was performed with the pure polymer to set a baseline. Storage modulus was the main concern in the experimentation because of its elastic nature. In Figure 4-3 storage and loss moduli for the pure polymer are shown. Initially, G' was higher at low frequency and increased with the increase in frequency. At higher frequency, G" became more prominent and G' started decreasing. For low frequency, elastic part was prominent and the viscous part started dominating at higher frequency.

Same experiment with the same frequency range, strain rate and temperature was performed for the three different concentrations of the surfactants. As the surfactant was non-ionic, it had no charge and no interaction was observed for each concentration of the surfactant. The surfactant concentration had much smaller effect and the storage and loss moduli were almost the same for all the concentrations. In Figure 4-4, all the three

concentrations along with the pure polymer are shown and all the graphs are overlapping. The surfactant solutions followed the same trend as for the pure polymer and in all the experiments, storage modulus was higher initially but started decreasing as frequency was increased. Figure 4-5 to Figure 4-7 represent the storage and loss modulus behavior against angular frequency.

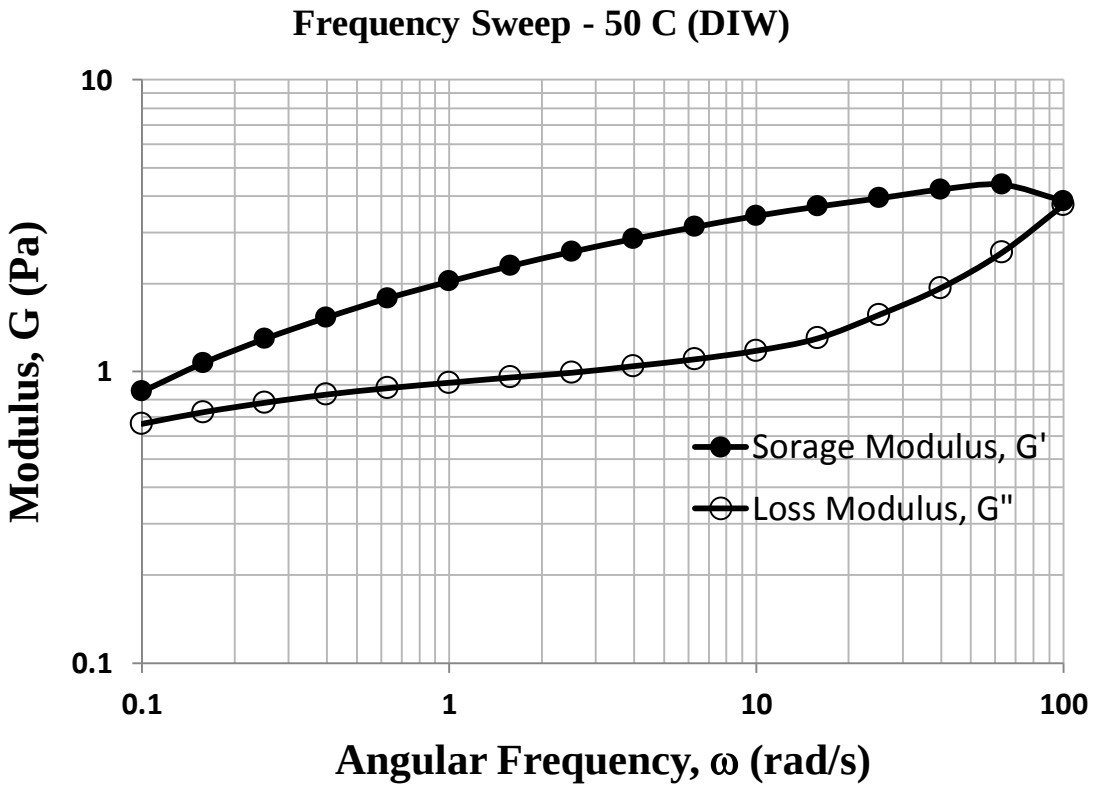


Figure 4-3 Storage Modulus and Loss Modulus vs Angular Frequency for HPAM soltuion

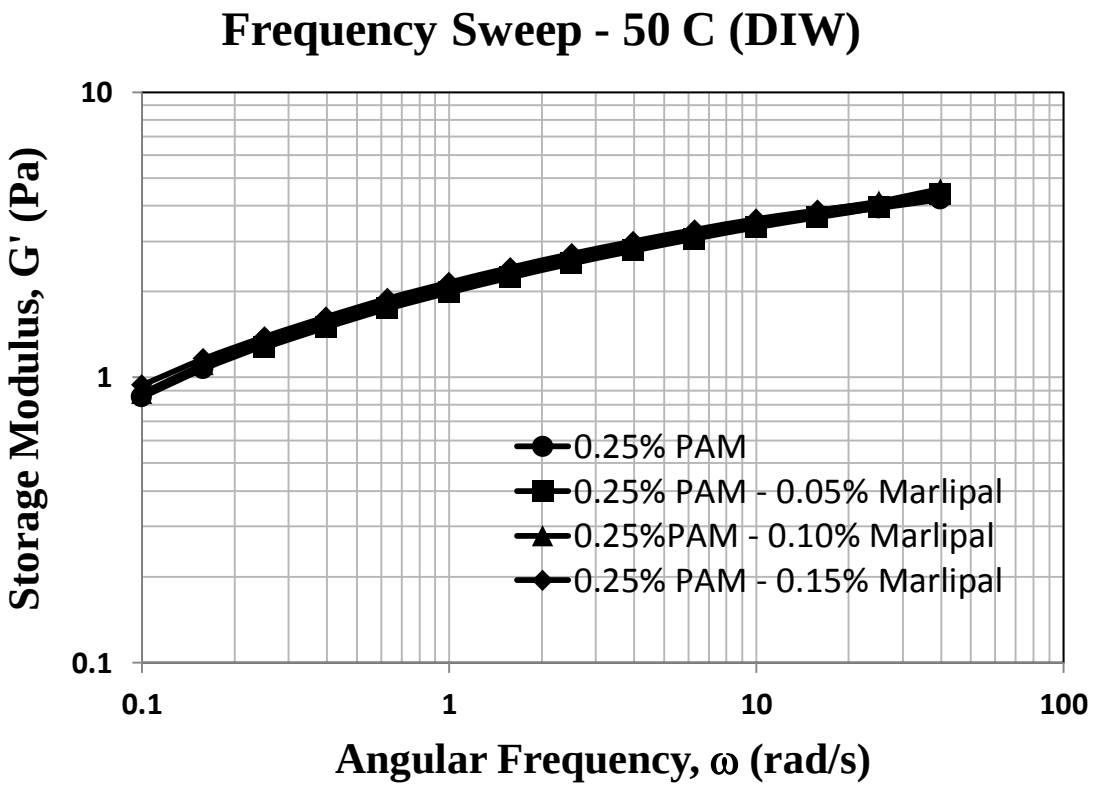


Figure 4-4 Storage Modulus vs Angular Frequency for HPAM Solution with different Marlipal O13/120 concentrations

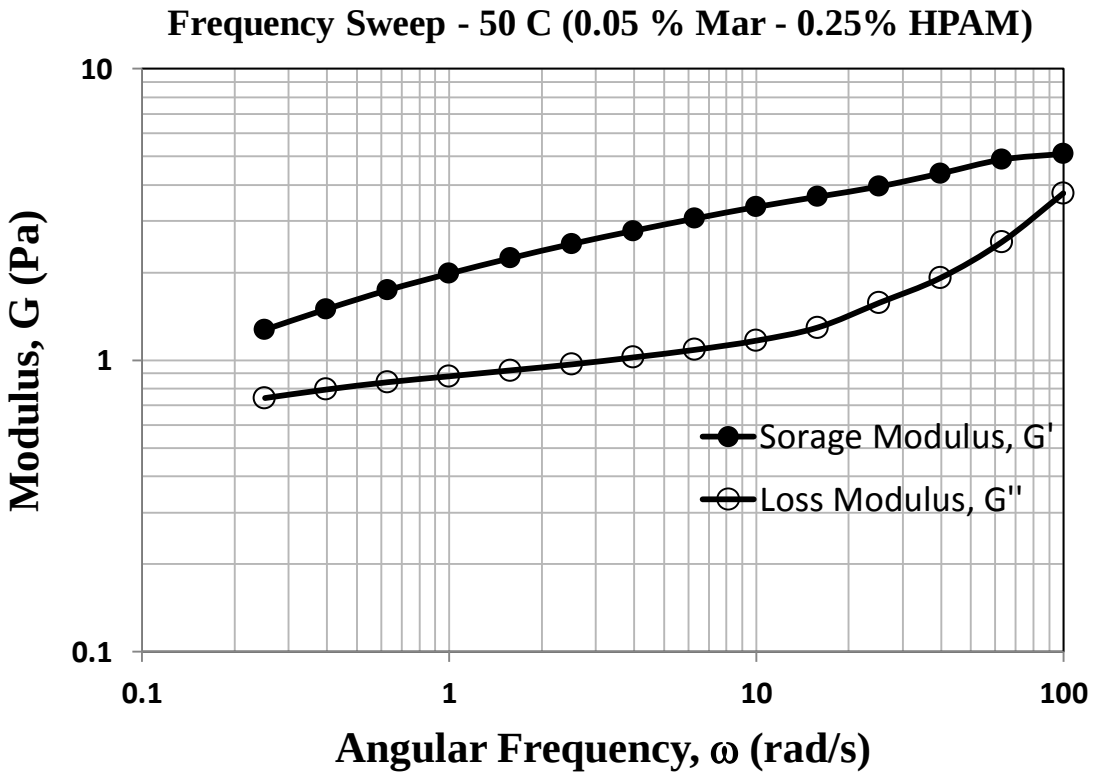


Figure 4-5 Storage and Loss Modulus vs Angular Frequency for HPAM with 0.05% Marlipal O13/120

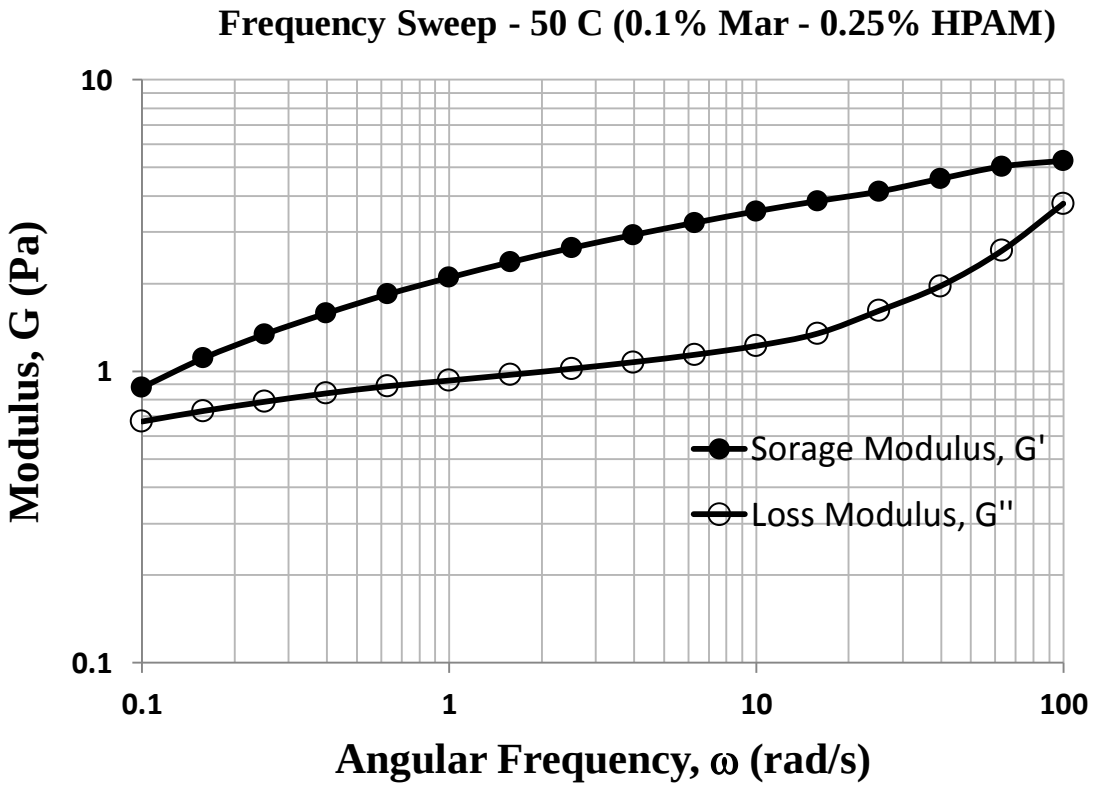


Figure 4-6 Storage and Loss Modulus vs Angular Frequency for HPAM with 0.10% Marlipal O13/120

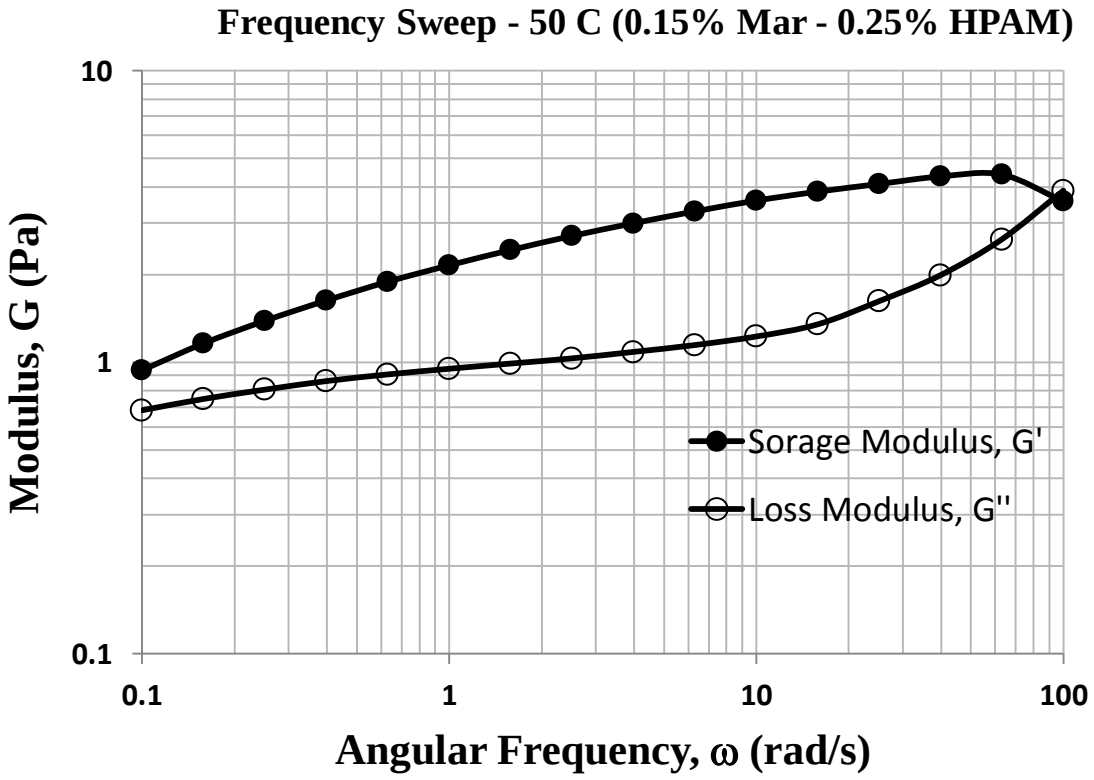


Figure 4-7 Storage and Loss Modulus vs Angular Frequency for HPAM with 0.15% Marlipal O13/120

Temperature Ramp:

Temperature ramp experiment was performed for the range of 30 to 90^{o}C and the shear rate was fixed at 0.01s^{-1}. The shear rate was fixed at low value to minimize its effect on the viscosity and thus, the only parameter affecting the viscosity will be the temperature. As the temperature was increased at a constant rate of 2^{o}C/min, the viscosity started decreasing. First experiment was performed for the pure polymer solution, the viscosity decreased with the increase in temperature. The viscosity profile against temperature is shown in the Figure 4-8.

After that, the temperature ramp experiment was performed for each concentration of the surfactant. It followed the same trend and the viscosity decreased with increasing the temperature. As shown in the Figure 4-8, all plots for different concentrations of the surfactant are overlapping. The bulk viscosity at any temperature is independent of the concentration of the surfactant. From the temperature ramp experiment, the main conclusion drawn was that the Marlipal had no charge and due to its non-ionic nature, it didn't affect the bulk viscosity of the polymer solution.

In the literature, it is stated that the surfactants decrease the viscosity and the polymers are added to increase the viscosity of the solution (Garry Pope, 2007). As this surfactant was not affecting the viscosity, it showed the ideal behavior and if this surfactant was able to decrease the IFT to the required level, it could simply be the best surfactant to use.

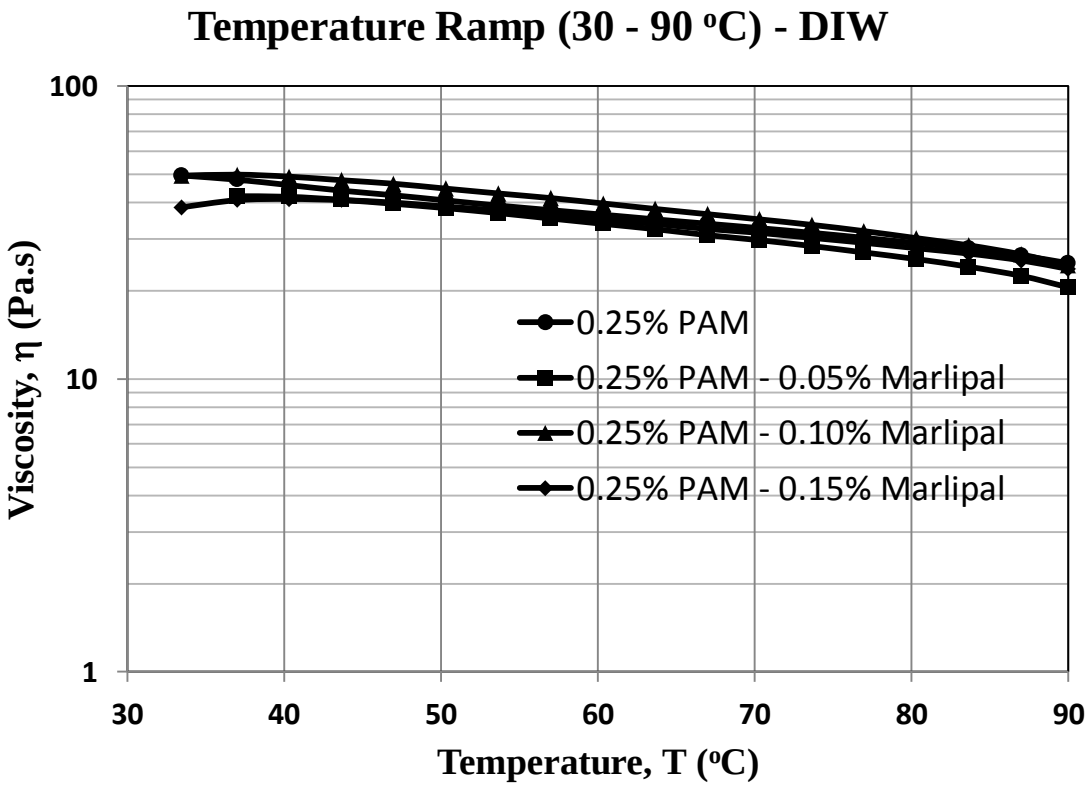


Figure 4-8 Temperature ramp for HPAM solution with different Marlipal O13/120 concentrations

System – 2:

Alfoterra 123-8s and HPAM:

The purity of Alfoterra was 88% consisting of water and small amount of solvent. The surfactant-polymer solutions were prepared with different concentrations in the same manner as for the previous system. The solution was prepared using DIW followed by the addition of the polymer and subsequently, the surfactant at the rim of the vortex at higher rpm. Sequence of the addition of the surfactant followed by the polymer had no effect on the rheological properties of the solution. The surfactant was added with the same concentrations of 0.05%, 0.1% and 0.15% and the polymer concentration was fixed at 0.25%. Equilibrium was achieved by keeping the prepared solution for 24 hours and after that the rheology experiments were performed.

Rheological data of the pure polymer was already acquired so the experiment started with the surfactant-polymer solution.

Flow Sweep:

All the parameters of this system were kept parallel with the previous system for the comparison purposes. Flow sweep experiments were performed at 50^{o}C and the shear rate range was defined to be .001 – 3000 s^{-1} for all the experiments. Flow sweep experiments were performed for the three different concentrations of Alfoterra with the polymer concentration being fixed at 0.25%. This surfactant was anionic in nature and thus, was expected to affect the bulk viscosity. Since the surfactant concentration was less significant than the polymer, this effect was expected to be smaller.

From Figure 4-9, it can be seen that after the addition of the surfactant, the bulk viscosity of the system starts to decrease. With the increase in the surfactant concentration; the decrease in the viscosity was proportional. So an inverse relationship between the surfactant concentration and the bulk viscosity was observed. Main reason behind this phenomenon was the presence of negative charge on the surfactant. Nasr-El Din (1991) reported similar behavior for the anionic surfactants and observed the decrease in the viscosity with the increase in the surfactant concentration. As the surfactant concentration was increased from 0.5 to 0.1%, a 30% decrease in the viscosity was observed at low shear rates. At the high shear rates at the typical reservoir conditions (10 - 50 s^{-1}), this decrease in the viscosity was reduced to 8% and both solutions showed roughly the same viscosity values. For the next concentration, the decrease was approximately 7% but still the viscosity value was much higher than the viscosity of water at the typical reservoir conditions.

It was observed that the main trend of the viscosity remained the same for this surfactant. At low shear rates, it somehow followed Newtonian behavior but as the shear rate was increased, the viscosity started decreasing linearly. At very high shear rates, it became Newtonian again and the viscosity approached the solvent viscosity which is DIW in this case. As this solution is power law fluid so it fits maximum models and these models depict that viscosity decreases with increasing the shear rate.

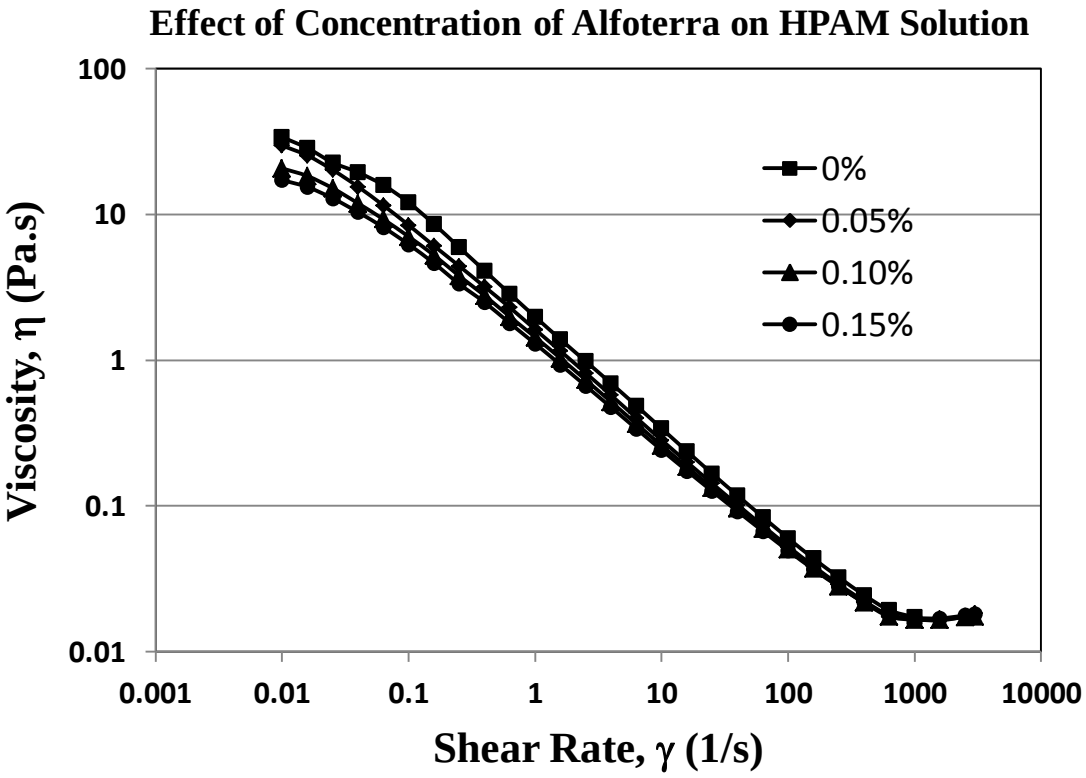


Figure 4-9 Viscosity vs shear rate for HPAM solution with different Alfoterra 123-8s concentrations

Frequency Sweep:

From the flow sweep experiments, the decrease in the bulk properties was observed as the surfactant concentration was increased and similar behavior was observed in the frequency sweep experiments. As the concentration of the surfactant was increased, storage modulus was observed to decrease and vice versa. However, the storage modulus increased with the increase in the frequency but after a critical frequency point, it started to decrease and the fluid started behaving as a viscous fluid. Similar trend was observed for all the plots but the only difference was that the plots shifted downward as the concentration of the surfactant was increased. When the concentration was increased from 0.05% to 1%, elasticity decreased roughly 17%. This effect was due to the long chain structure of the surfactant which influences the polymer structure. Polymer morphology was changed due to the incorporation of the surfactant. Maximum decrease in the elasticity was observed to be 42% when 0.15% of the surfactant was added to the pure polymer solution. Storage and loss moduli for all the concentrations and for the pure polymer are shown in Figure 4-10. Similar trend was observed with the loss modulus plot. It was due to the overall decrease in the viscoelastic properties of the polymer solution and the solution morphology variations with the addition of the surfactant. Figure 4-11 shows the plot of loss modulus for the different concentrations of Alfoterra with 0.25% HPAM.

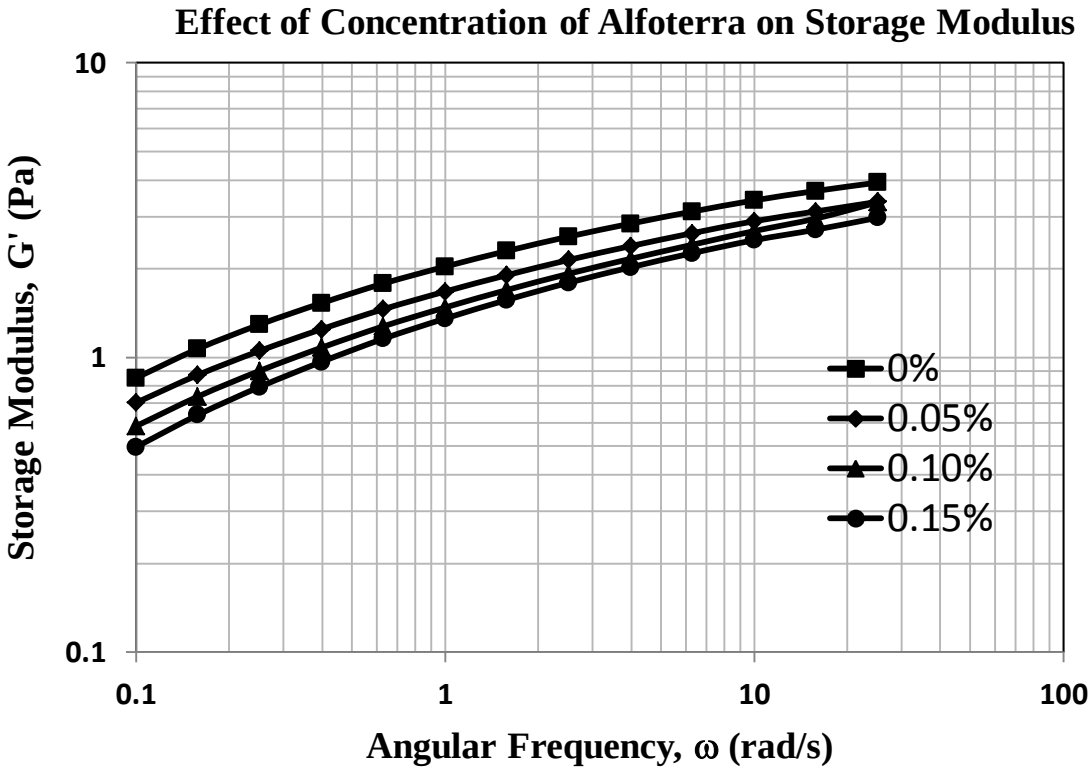


Figure 4-10 Storage modulus vs angular frequency for HPAM solution with different Alfoterra 123-8s concentrations

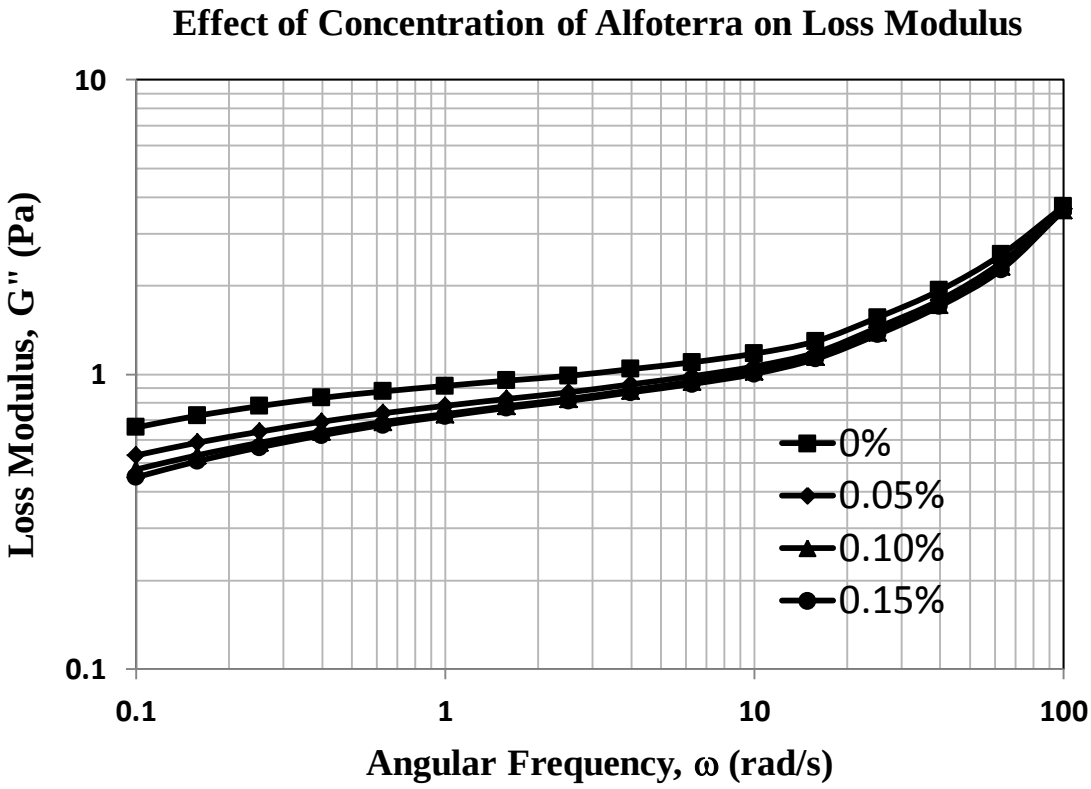


Figure 4-11 Loss modulus vs angular frequency for HPAM solution with different Alfoterra 123-8s concentrations

Temperature Ramp:

This test was performed to study the effect of the concentration on the rheological properties during the temperature increase. According to the manufacturer, this surfactant was thermally unstable when tested at high temperature. But this experiment was performed for only a short duration and the surfactant was used in the solution. The surfactant degradation was reduced due to the presence of the polymer. The surfactant-polymer solution was not much affected by the temperature. It followed the same trend as for the pure polymer and for the other systems. The only noticeable thing was the decrease in the viscosity as the concentration was increased. The experiments were performed for different concentrations of the surfactant whereas the polymer concentration was kept constant. When the concentration of the surfactant was increased, the plot shifted down a little bit, but the trend of decrease in the viscosity with the increasing temperature remained the same as for the previous systems. Temperature change rate was again kept constant at 2^{o}C/min. From Figure 4-12, it is shown that for high temperature, this system of surfactant-polymer worked fine. No degradation or sudden decrease or increase in the viscosity was observed which showed that when the surfactant without aging was used with the polymer in solution, it will work fine.

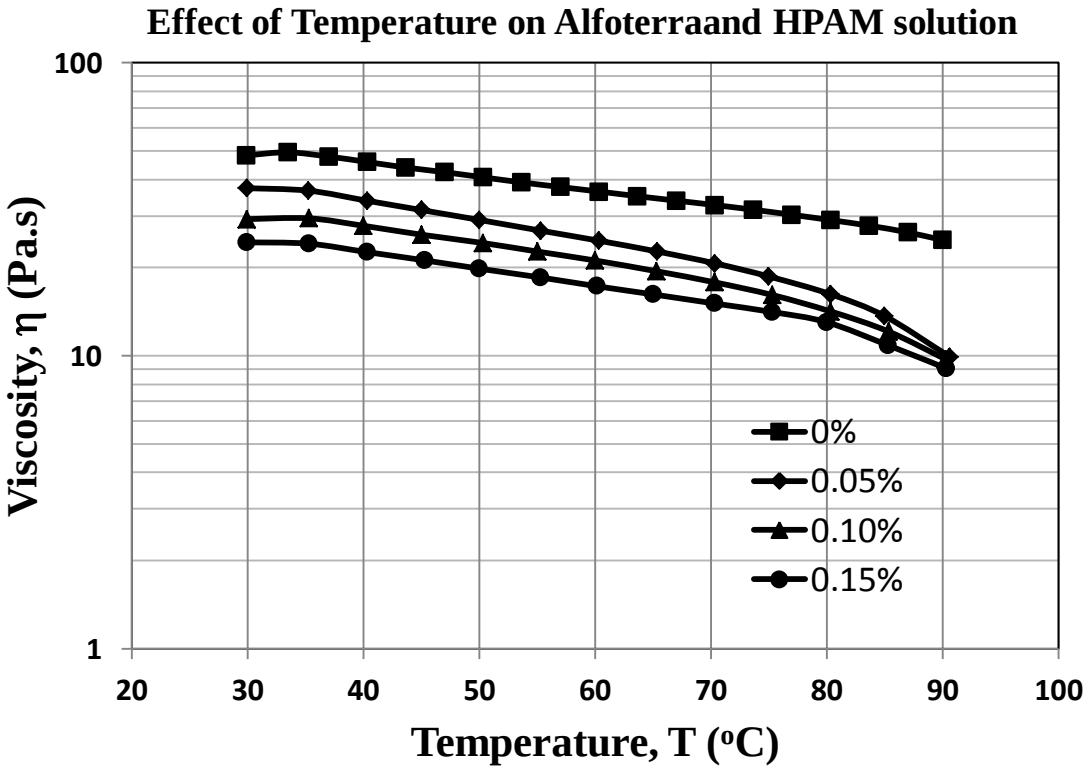


Figure 4-12 Temperature ramp for HPAM solution with different Alfoterra 123-8s concentrations

4.3.2: Effect of Temperature:

System – 1:

Marlipal O13/120 and HPAM:

Temperature affects the polymer more than the surfactant, as the surfactants had no significant effect on the bulk properties in the solution. The surfactant could be degraded alone but in the solution with the polymer, no degradation was observed. This experiment was performed to check the thermal stability of the polymer-surfactant solution. The viscosity was decreasing mainly because of the polymer. Our major concern was to observe the decrease in the viscosity with the increase in the temperature.

The experiments were performed both at high and low temperatures to find out if there was an abrupt change in the viscosity of the solution. The solutions were not aged and when tested at high temperature, there was a decrease in the viscosity which was still much higher than the viscosity of water. Other reason for the decrease in the viscosity of the polymer solution was hydrolysis of the HPAM. The polymer could be hydrolyzed more if it was aged at higher temperature but in this experiment, the hydrolysis did not played a major role. For the pure polymer, at higher temperature the decrease in the viscosity was observed but it was still much higher than the viscosity of the water at typical reservoir conditions. Seright et al (2009) reported the similar trend of the decrease in the viscosity at higher temperature. This trend is shown in the Figure 4-13 to Figure 4-16. For low shear rate, 30% decrease in the viscosity was observed at $90^{o}C$ but at the typical reservoir conditions (10 – 50 s^{-1}), similar viscosity was observed at both temperatures.

The frequency sweep experiment was performed to observe the effect of the temperature on the viscoelastic properties. The elastic properties of the solution decreased at higher temperature. Figure 4-17 to Figure 4-19 show the plots for the surfactant concentrations of 0.05%, 0.1% and 0.15% respectively. At low angular frequency, about 20 – 25% decrease in the storage modulus was observed for each concentration. Decrease in the elastic properties was observed because of the polymer as the surfactant had no effect on the bulk and viscoelastic properties of the solution.

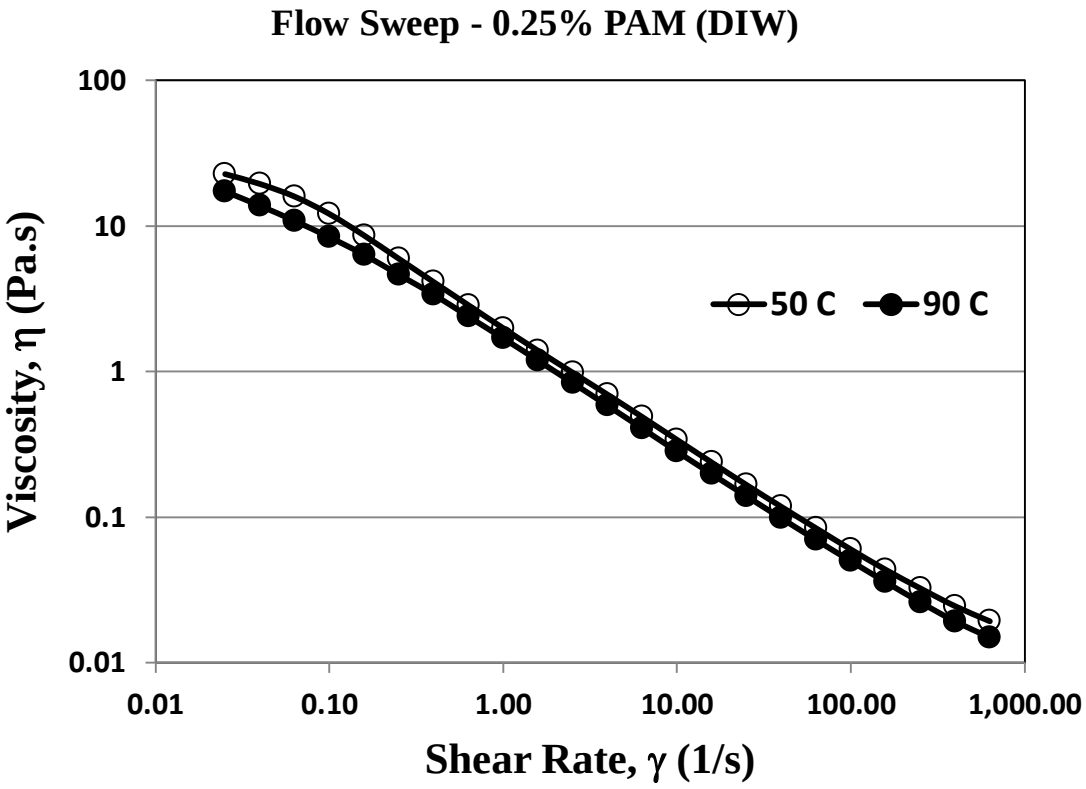


Figure 4-13 Effect of temperature on the viscosity of HPAM solution

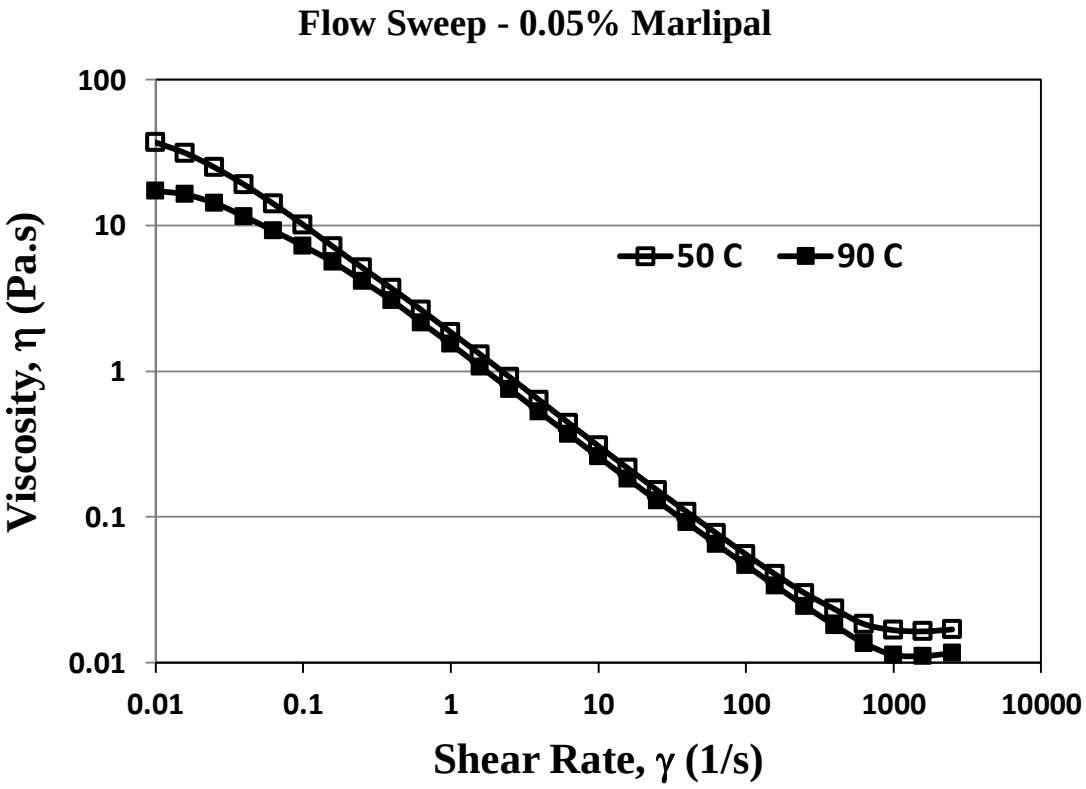


Figure 4-14 Effect of temperature on the viscosity of HPAM solution with 0.05% Marlipal O13/120

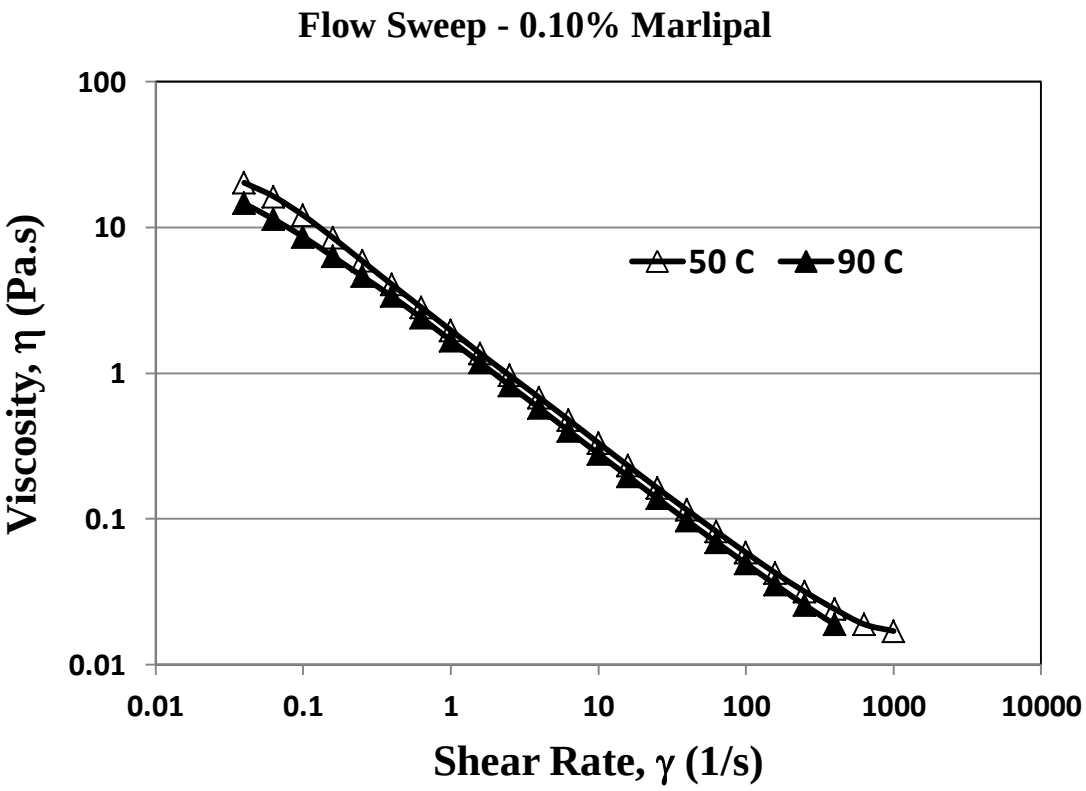


Figure 4-15 Effect of temperature on the viscosity of HPAM solution with 0.10% Marlipal O13/120

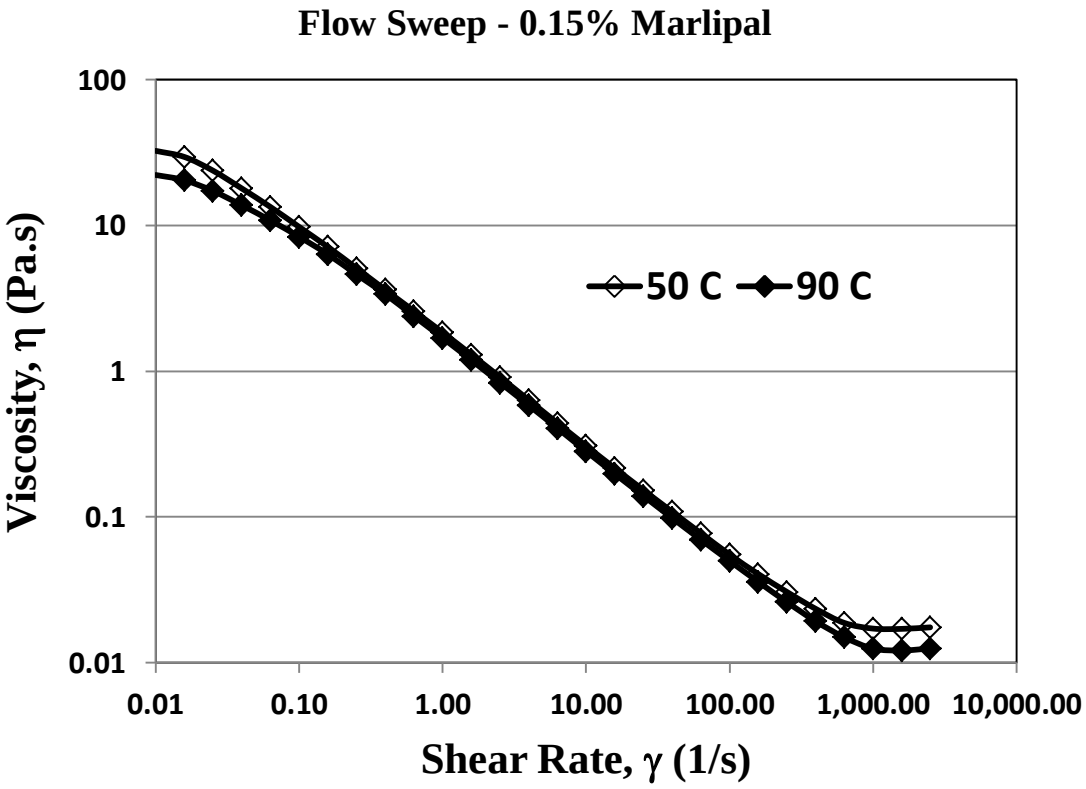


Figure 4-16 Effect of temperature on the viscosity of HPAM solution with 0.15% Marlipal O13/120

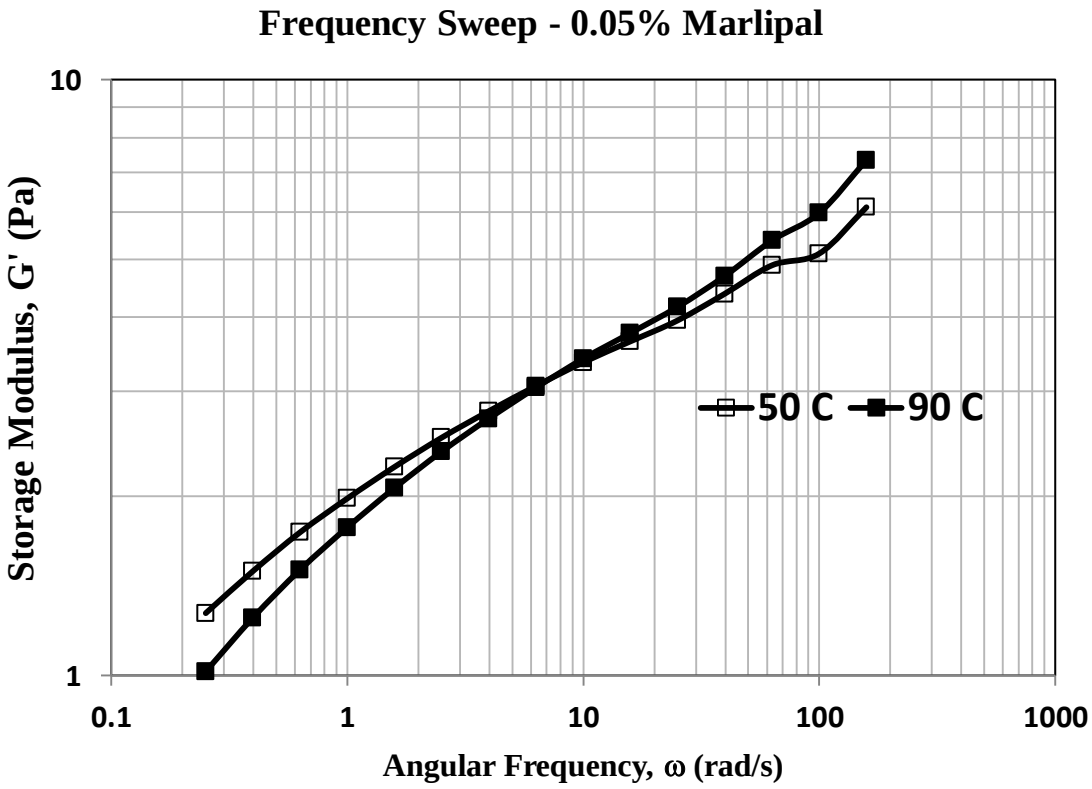


Figure 4-17 Effect of temperature on the storage modulus of HPAM solution with 0.05% Marlipal O13/120

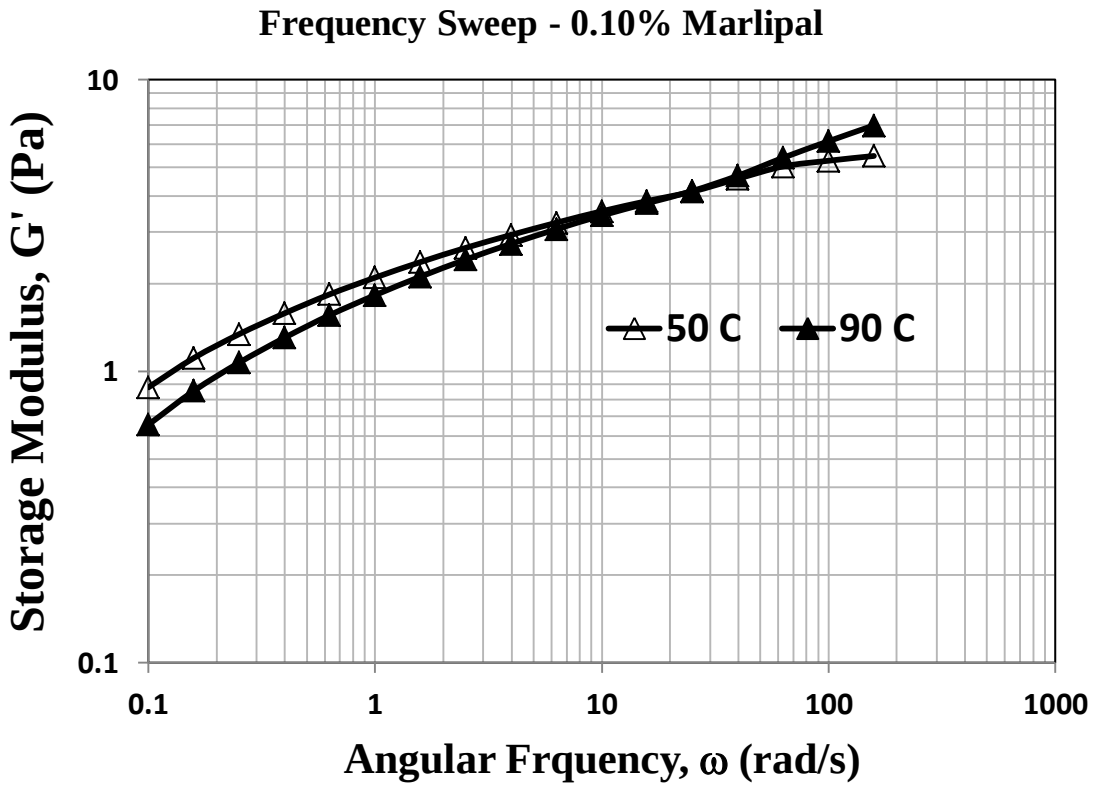


Figure 4-18 Effect of temperature on the storage modulus of HPAM solution with 0.10% Marlipal O13/120

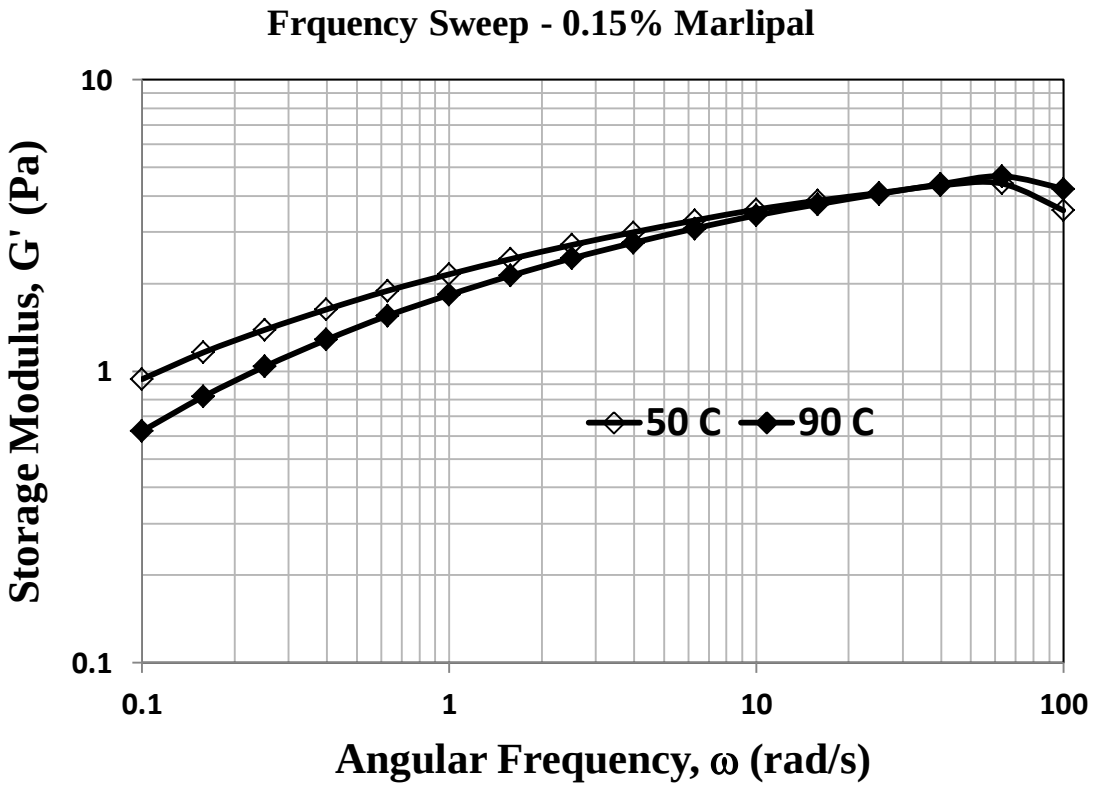


Figure 4-19 Effect of temperature on the storage modulus of HPAM solution with 0.15% Marlipal O13/120

System – 2:

Alfoterra 123-8s and PMMA 2530s:

This experiment was performed to observe the effect of the temperature on the solution viscosity of Alfoterra and HPAM. For the pure polymer with the increase in the temperature, the viscosity decreased. The experiments were performed at two different temperatures (50^{o}C and 90^{o}C) and the polymer concentration used was 0.25%. The experiment was repeated for the different concentrations of Alfoterra. Same results were observed in the presence of the surfactant and the viscosity was decreased at higher temperature. At low shear rates, 30 – 35% decrease in the viscosity was observed for each concentration whereas the viscosity was similar at the typical reservoir conditions. The viscosity trend was the same for each concentration but shifted downward at higher temperatures. At high shear rates, the viscosity was almost the same for both temperatures as the shearing effect was greater than the effect of the temperature. Figure 4-20 to Figure 4-22 show the plots for the temperature effect on the different concentrations of the surfactant.

For the frequency sweep, results were similar to the system of Marlipal and HPAM. Figure 4-23 to Figure 4-25 show the storage modulus against the angular frequency for the two different temperatures. At low frequency, the viscoelastic properties of the system also reduced and 25 – 30% decrease in the viscosity was observed for each concentration. At higher temperature, bulk properties of the solution reduced which was the reason behind the decrease in the storage modulus.

Overall, the effect of temperature on both the systems was almost the same. In the case of concentration, the increased concentration decreased the bulk properties for the second system.

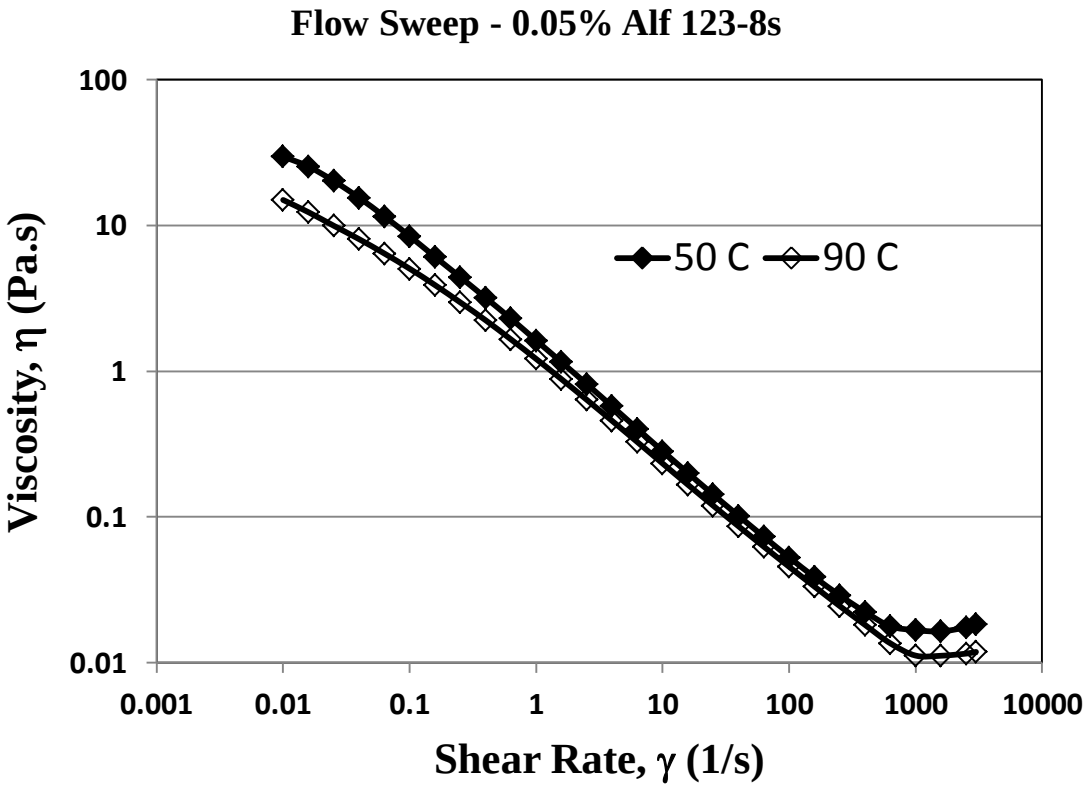


Figure 4-20 Effect of temperature on the viscosity of HPAM solution with 0.05% Alfoterra 123-8s

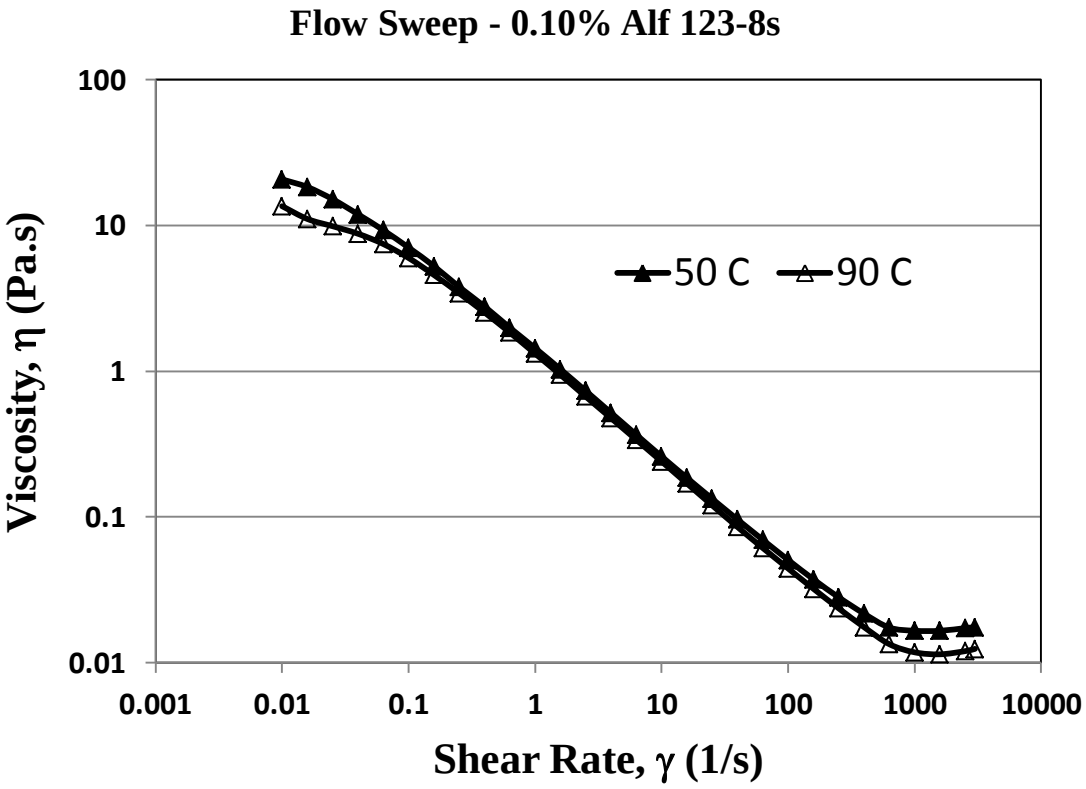


Figure 4-21 Effect of temperature on the viscosity of HPAM solution with 0.10% Alfoterra 123-8s

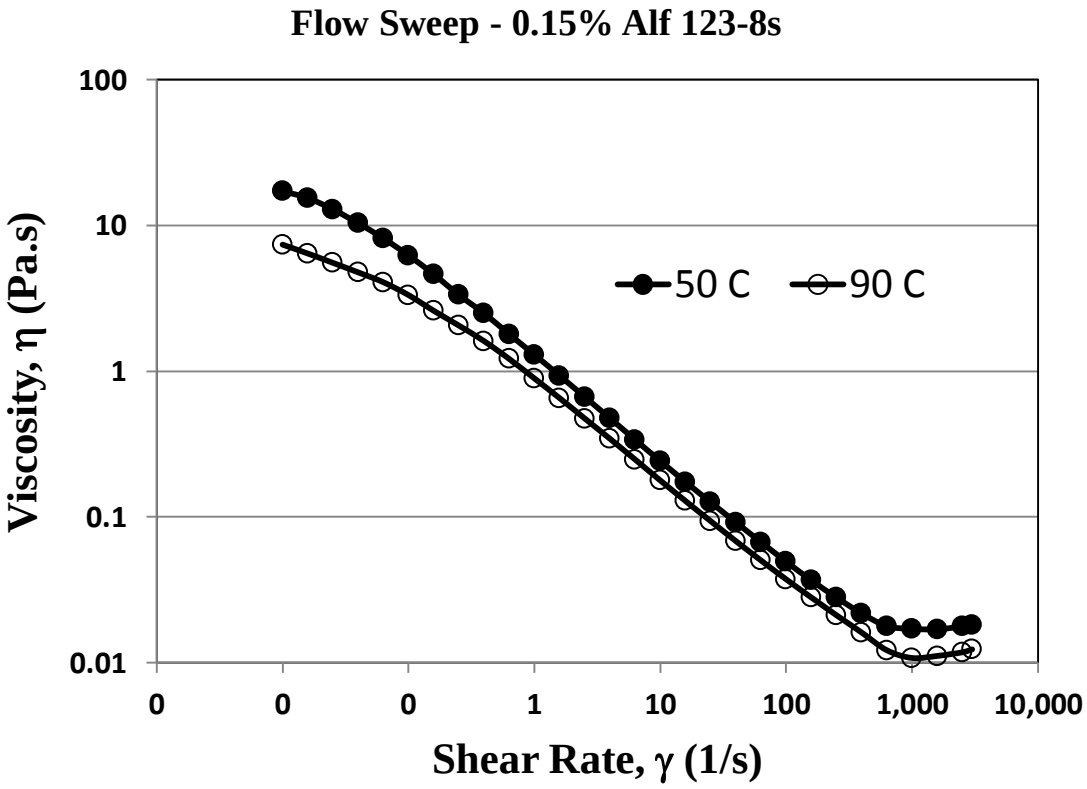


Figure 4-22 Effect of temperature on the viscosity of HPAM solution with 0.15% Alfoterra 123-8s

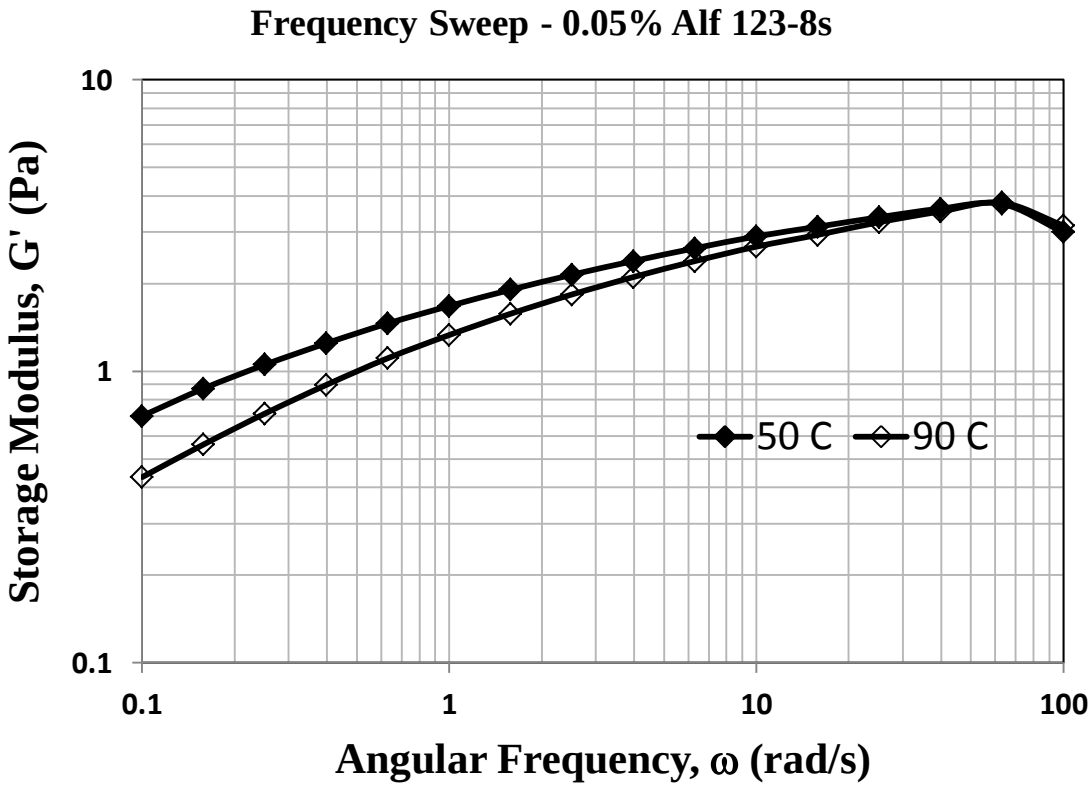


Figure 4-23 Effect of temperature on the storage modulus of HPAM solution with 0.05% Alfoterra 123-8s

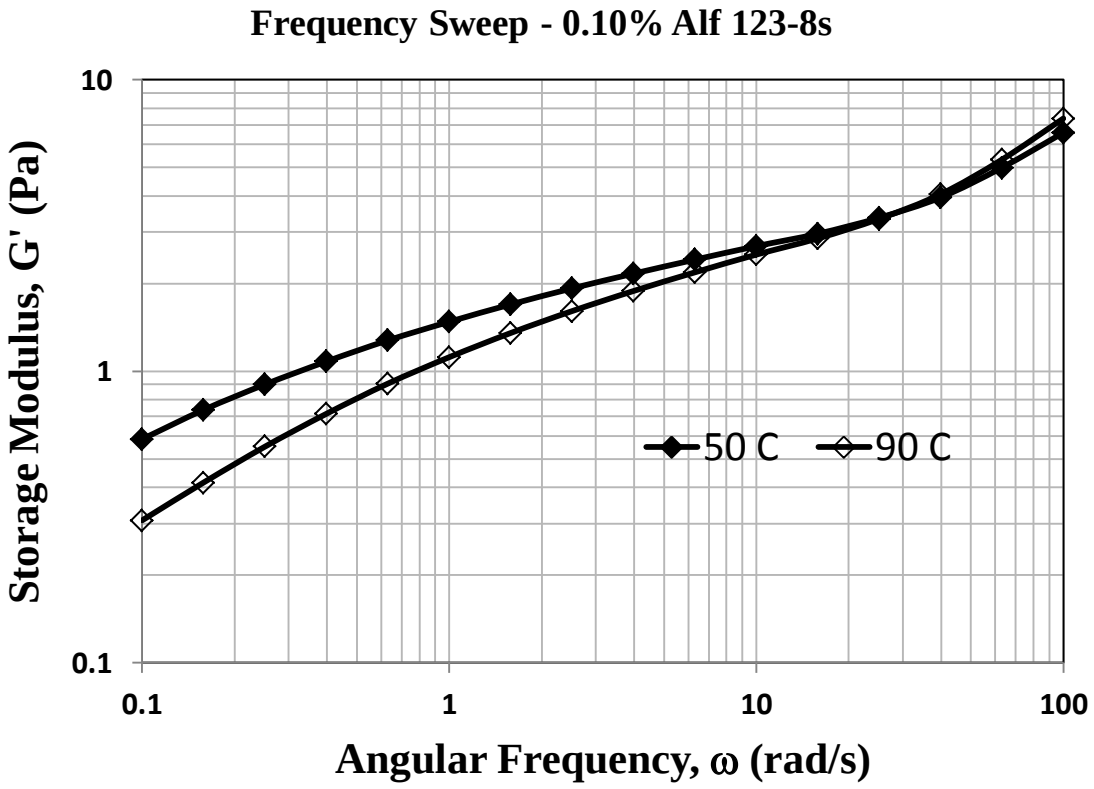


Figure 4-24 Effect of temperature on the storage modulus of HPAM solution with 0.10% Alfoterra 123-8s

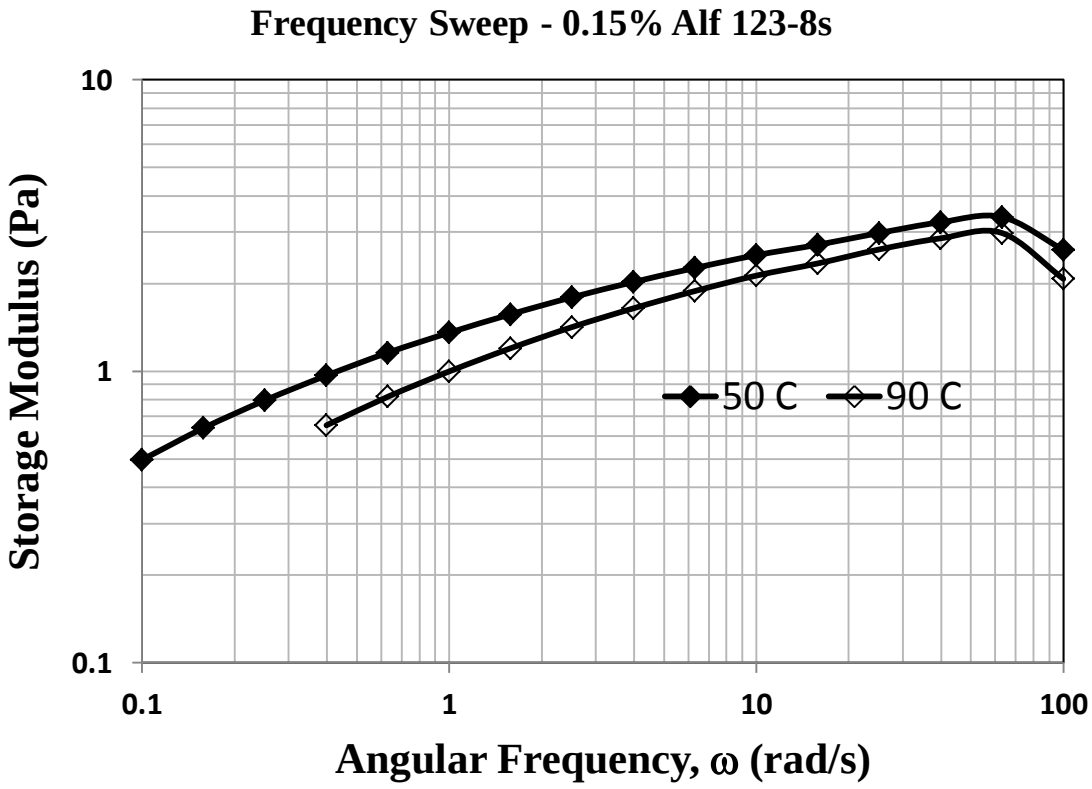


Figure 4-25 Effect of temperature on the storage modulus of HPAM solution with 0.15% Alfoterra 123-8s

4.3.3: Effect of Salinity:

During rheology experimentation, the main parameter to study was the effect of salinity on the solution. Literature explained that the polymer was not capable to withstand high salinity (Taylor, 1995). In this work, the major focus was on the surfactant as we had fixed the polymer concentration. Different salinities were used for a single concentration of the surfactant and the polymer to observe the effect of salinity.

Three solutions with the salinities of 57,000 ppm, 114,000 ppm and 228,000 ppm were prepared. The polymer concentration used was 0.25% and the surfactant concentration used was 0.1% which was the optimum between the three concentrations used previously. The solutions were prepared and checked for the compatibility tests and no precipitation was observed for both the surfactants.

The only flow sweep experiment that was performed to observe the effect of the salinity on the viscosity of the solutions. The experiment was performed at low temperature ($50^{o}C$) for both the systems to avoid the effect of temperature on the viscosity. For the minimum salinity (57,000ppm), dramatic decrease in the viscosity was observed for both systems. The presence of monovalent ions (Na+) and divalent ions (Mg++, Ca++) caused the charge shielding effect and reduced the hydraulic radius of the polymer chains which resulted in the decrease of the viscosity. Mandel et al. (2008) and Bataweel et al. (2009) had reported this behavior. Three different salinities were used for Marlipal but for Alfoterra, the minimum salinity was used to see the effect of the salts. For Marlipal, all the three salinities showed similar reduction in the viscosity. Figure 4-26 shows the effect of the salts on the solution of Marlipal and HPAM. Although the reduction was large but the viscosity was still ten times higher than the viscosity of water (0.001 Pa.s) at the

typical reservoir conditions. Similarly, Figure 4-27 shows the effect of the salts on the solution of Alfoterra and HPAM. Major reduction in the viscosity was due to the polymer as Marlipal had no effect on the bulk properties and Alfoterra had only a small effect. Interaction between the salts and the surfactant molecules had minimum effect on the viscosity.

From the rheology experiments, it was concluded that at the reservoir conditions ($T=90^{o}C$, shear rate = $10s^{-1}$, salinity = 57000 ppm) both systems had the viscosity of 0.01 Pa.s which was ten times higher than the water viscosity (0.001 Pa.s). Marlipal had no effect on the bulk properties of the solution but Alfoterra had a small effect. Marlipal concentration had no effect on the viscosity and the elastic properties of the system. Alfoterra reduces the viscosity and elastic properties as its concentration was increased. Both systems showed promising results in thermal stability test and no degradation was observed during these tests. The SP systems had issues against salts but major problem was due to polymers as the surfactants were not much affected with the salts. Optimum concentration of the surfactants would be found out from the IFT experiments and will be used in the core flooding experiments. Both systems had no issue of the compatibility with the salts and both could be used for core flooding.

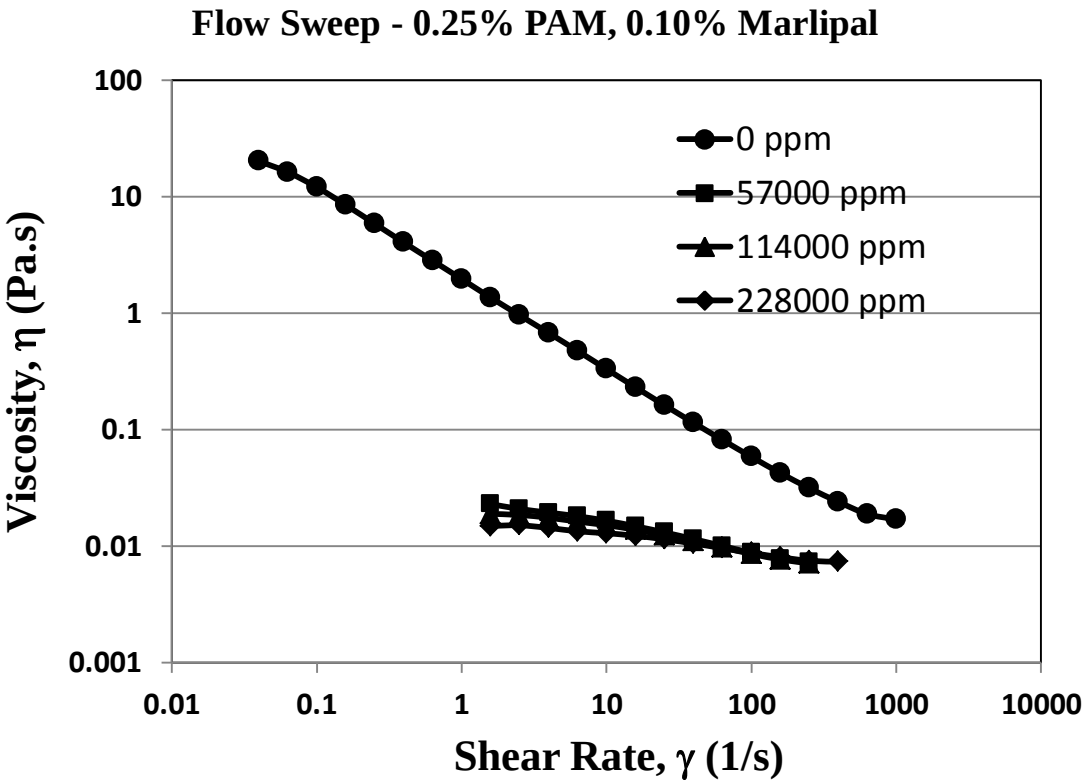


Figure 4-26 Effect of salts on the viscosity of HPAM solution with 0.10% Marlipal O13/120

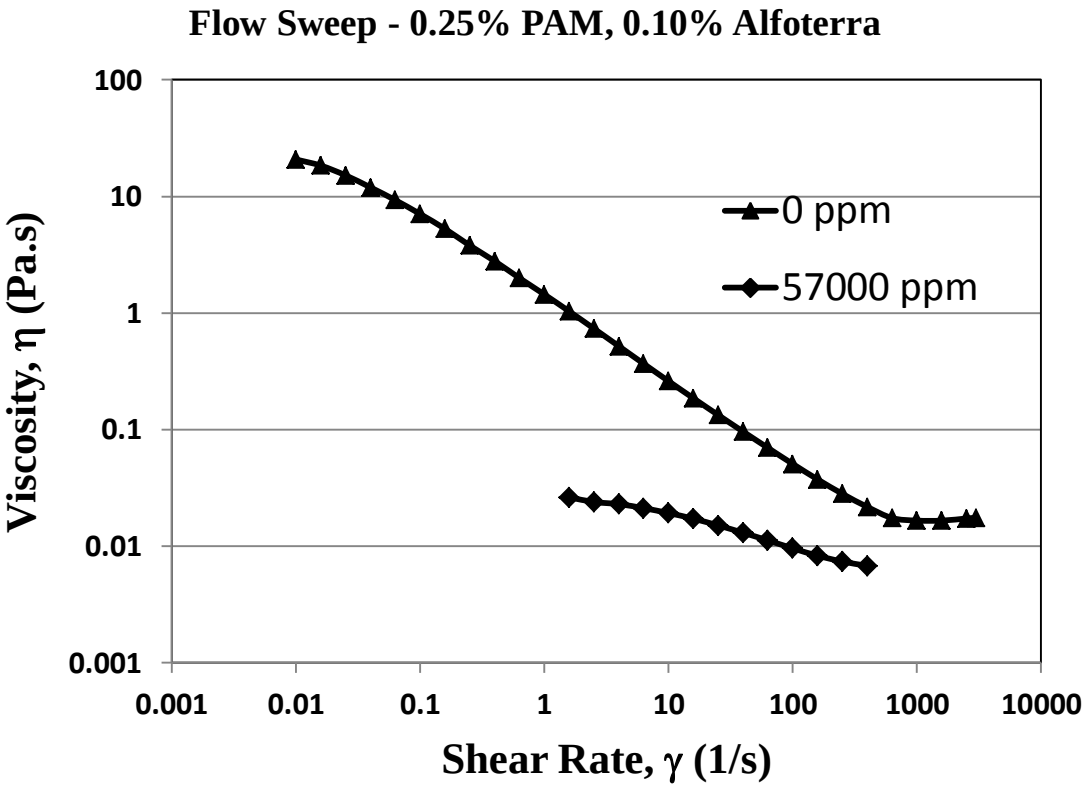


Figure 4-27 Effect of salts on the viscosity of HPAM solution with 0.10% Alfoterra 123-8s

4.4: Thermal Stability:

Thermal stability experiments were performed for the pure surfactants to check their stability and categorize them for particular conditions. In the rheology experiments, salinity affected the solutions but the temperature effects were not prominent. Second stage was to investigate the thermal stability of the pure surfactants. FTIR and NMR techniques were used to analyze the samples before and after aging. TGA was also used to check the stability of the surfactants without aging. These techniques were not used in the past and no references were available for the surfactants in the literature.

4.4.1: Thermo Gravimetric Analyzer (TGA) Results:

This experiment was performed to investigate the behavior of the surfactants towards the temperature increase. According to the data provided by the manufacture, Marlipal was thermally stable but Alfoterra was not suitable for high temperature applications. Figure 4-28 shows the plot of weight loss versus temperature for Marlipal. No weight loss was observed for Marlipal up to 180^{o}C. No solvent or impurities were present that could have made the surfactant thermally stable up to high temperature. Major weight loss was observed after 350^{o}C and the reservoir temperature is around 110^{o}C. Degradation could be due to the breakage of hydrogen-carbon bonds at high temperature which occurred after 350^{o}C. Marlipal is considered to be thermally a very strong surfactant and a promising candidate for the high temperature reservoirs. On the other hand, Alfoterra was 88% pure and contained water and solvent contents. Figure 4-29 shows the trend for weight loss versus temperature for Alfoterra. Small decrease in the weight was observed at 110^{o}C which was due to the evaporation of water and solvent contents present in the sample and the weight was reduced to 92%. Major change in the weight loss was

observed after 190^{o}C and the surfactant was totally degraded after 190^{o}C. Thermal degradation in Alfoterra could be due to the breakage of carbon-sulfate bonds. This experiment was performed for a short period and both the surfactants showed promising results. Marlipal was more stable than Alfoterra but for a short period, Alfoterra also showed excellent results. Both the surfactants were tested for a long period and other techniques were used to analyze the thermal degradation at high temperature.

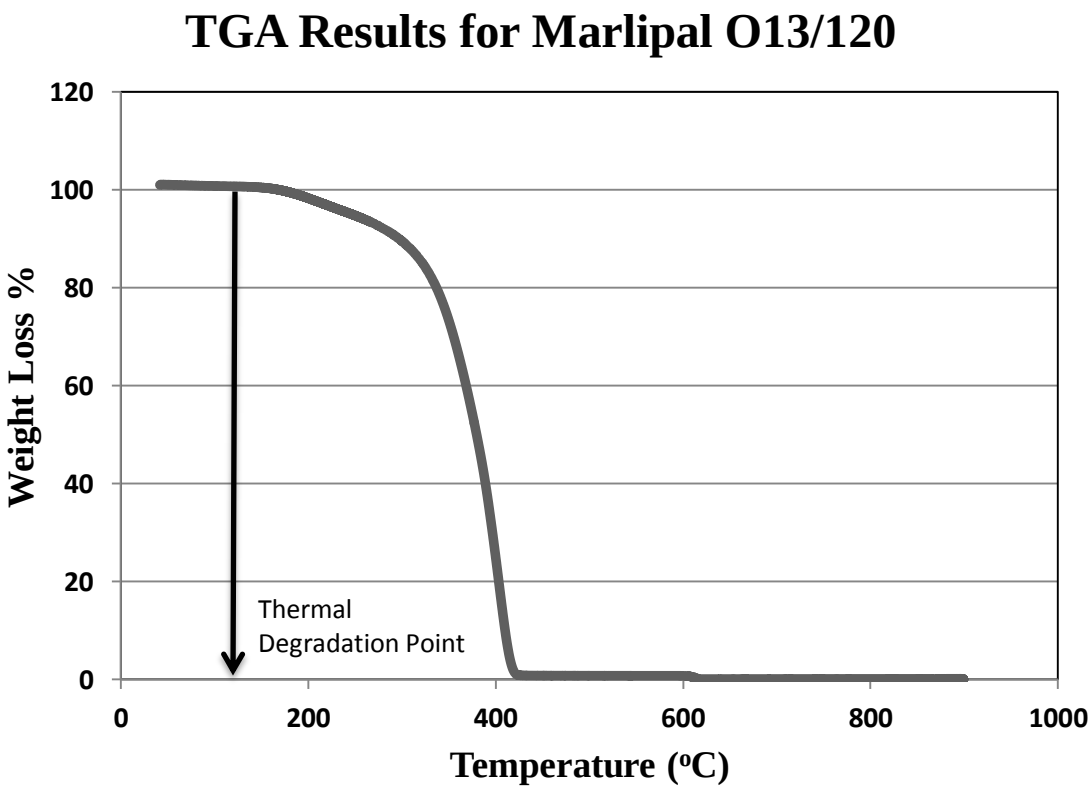


Figure 4-28 TGA analysis for Marlipal O13/120

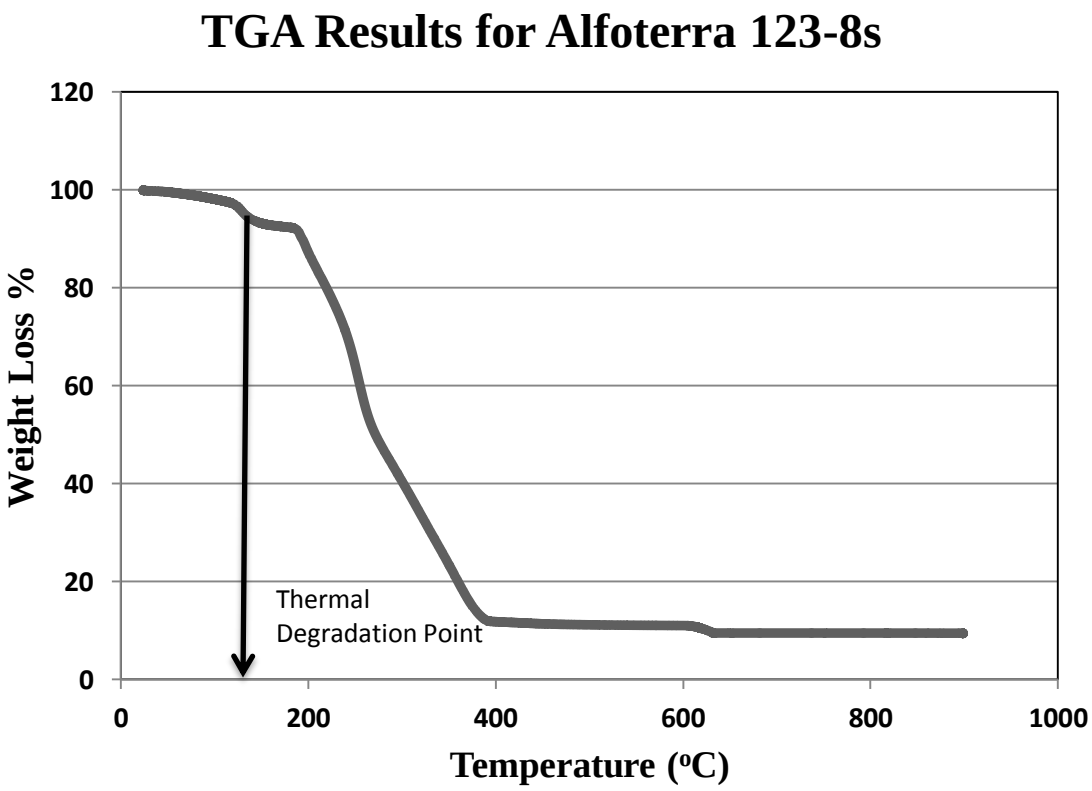


Figure 4-29 TGA analysis for Alfoterra 123-8s

4.4.2: FTIR Results:

The Surfactant samples were aged at 80^{o}C in the oven for 1, 3 and 7 days and investigated using FTIR to observe if there were any structural changes after aging. Marlipal showed no physical change even after 7 days but Alfoterra was degraded after 24 hours. Figure 4-30 shows the FTIR results for four samples of Marlipal aged for 1, 3 and 7 days. Comparison of the spectrum for the aged and non-aged samples shows that no structural changes occurred even after 7 days aging at high temperature. It also shows that the surfactant was much more stable at high temperature for a longer period of time. Marlipal is considered to be a thermally stable surfactant and a promising candidate for high temperature applications. Aging for Alfoterra was stopped after 24 hours as physical degradation was observed in the sample. When analyzed through FTIR, two different spectrums were observed for the aged and non-aged samples of Alfoterra. Figure 4-31 shows the spectrum for these two samples of Alfoterra. Some structural changes occurred in the surfactant and this could be due to the breakage of weak bonds. Main changes that occurred were the increase in the carboxyl groups and some change in the functional groups was also observed. For detailed analysis, NMR technique was used to study the thermal degradation of Alfoterra.

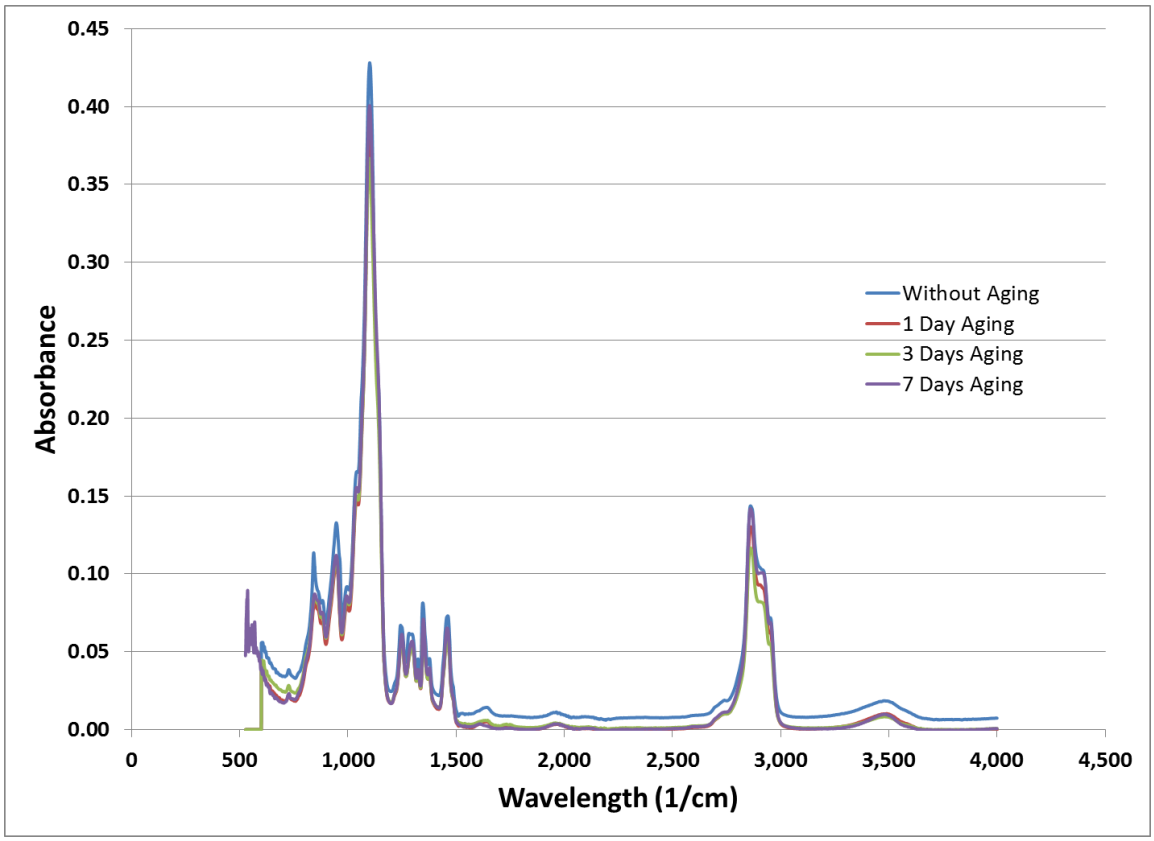


Figure 4-30 FTIR analysis for Marlipal O13/120

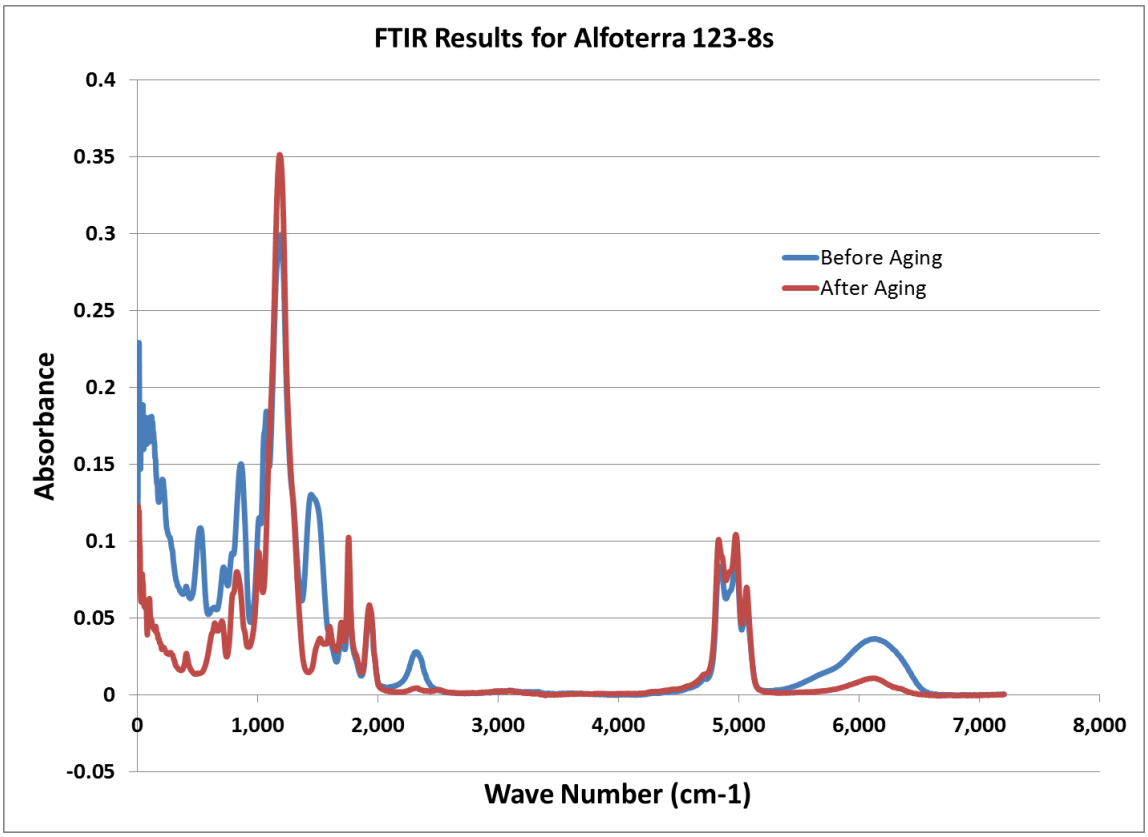


Figure 4-31 FTIR analysis for Alfoterra 123-8s

4.4.3: NMR Results:

Detailed study of the thermal stability of the surfactants was done by performing NMR experiments for the same aged samples. Figure 4-32 and Figure 4-33 show the results of Proton NMR experiment for Marlipal. This experiment was performed to investigate if there was a change in the number or position of hydrogen from one molecule to another. Results show that all peaks were almost the same and there were only some minor changes in the spectrums. The surfactant didn't undergo any structural or chemical change even after 7 days of aging and the spectra were almost the same for both samples. Figure 4-34 and Figure 4-35 show the results for Carbon NMR experiment performed for Marlipal to investigate the number and changes in the functional groups occurred after aging. The results show that all the functional groups sustained original places and no change in the spectrums was observed. After the results obtained from all these experiments of Marlipal, it was considered as thermally stable and a good option for high temperature applications. When NMR experiments were performed for Alfoterra, different spectra were obtained for both proton and carbon NMR. Figure 4-36 and Figure 4-37 show the results for proton NMR of Alfoterra samples before and after aging, respectively. Proton NMR explained that the changes occurred in the position of hydrogen molecules. Different spectra showed that the hydrogen molecules were shifted from one functional group to another. Figure 4-38 to Figure 4-39 show the spectra of carbon NMR for Alfoterra samples before and after aging. Before aging, there were 7 major peaks showing the presence of carbon molecules in 7 different chemical environments. Chemical shift was in the range of 14 to 75 ppm. After aging, the number of peaks reduced to 6 representing the presence of carbon atom now in 6 different chemical environments. Chemical shift range was almost similar from 18 to 75 ppm but

there was no chemical shift in the range of 20 – 35 ppm. Also the intensity of carbon, with chemical shift between 70 – 75 ppm, increased and showed that the number of ether groups increased after aging. In the lower range of chemical shift, the intensity of peaks increased which explains that $CH_3$was either converted to CH_2 or CH_3-O. NMR results revealed that with aging at higher temperature, number of ether groups was increased and C-H converted to C-O bonds resulting in thermal degradation of the Alfoterra.

From thermal stability experiments it is concluded that Marlipal is much more stable for both short period and long period applications. On the other hand Alfoterra was stable or short period aging and degraded in long period aging experiments. Marlipal will produce more promising results for high temperature applications.

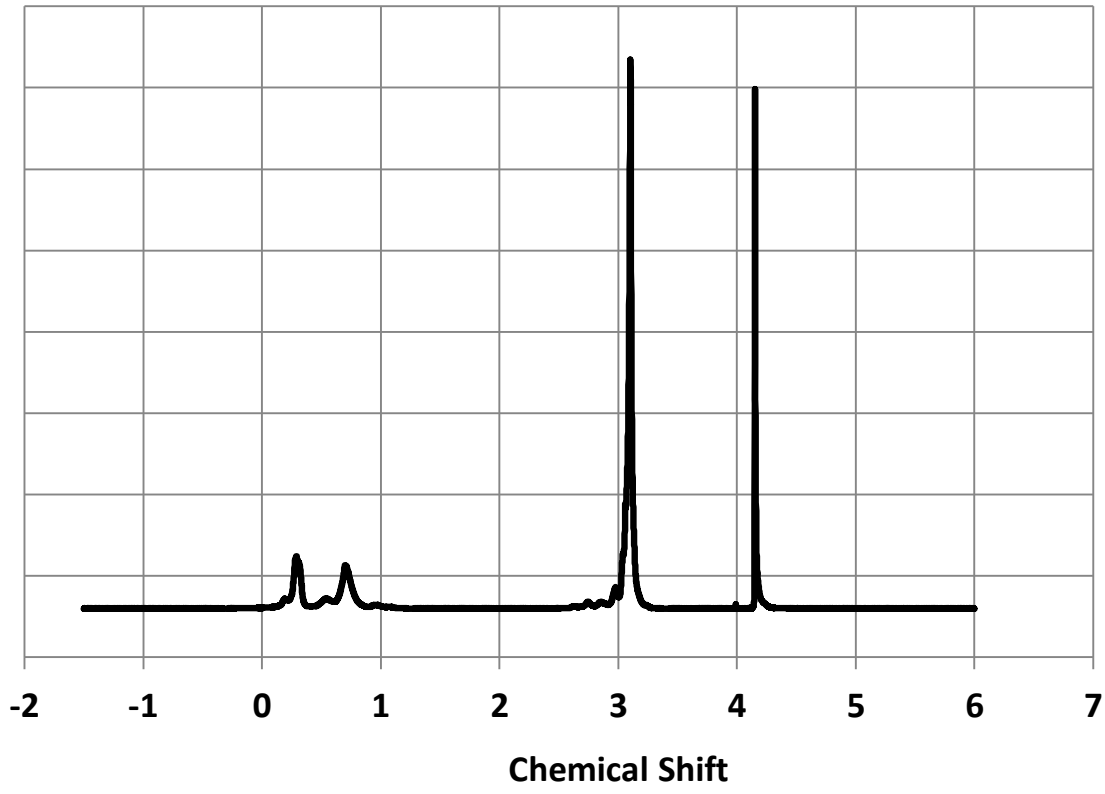


Figure 4-32 NMR-H results for Marlipal O13/120 before aging

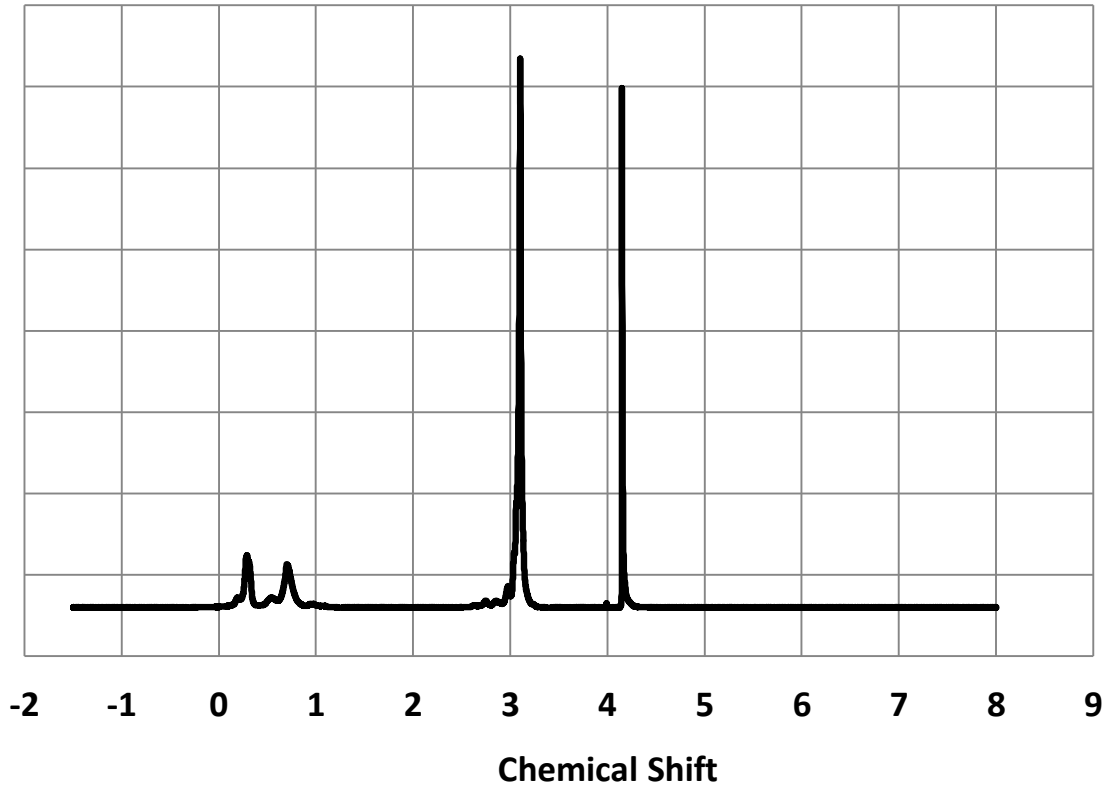


Figure 4-33 NMR-H results for Marlipal O13/120 after aging

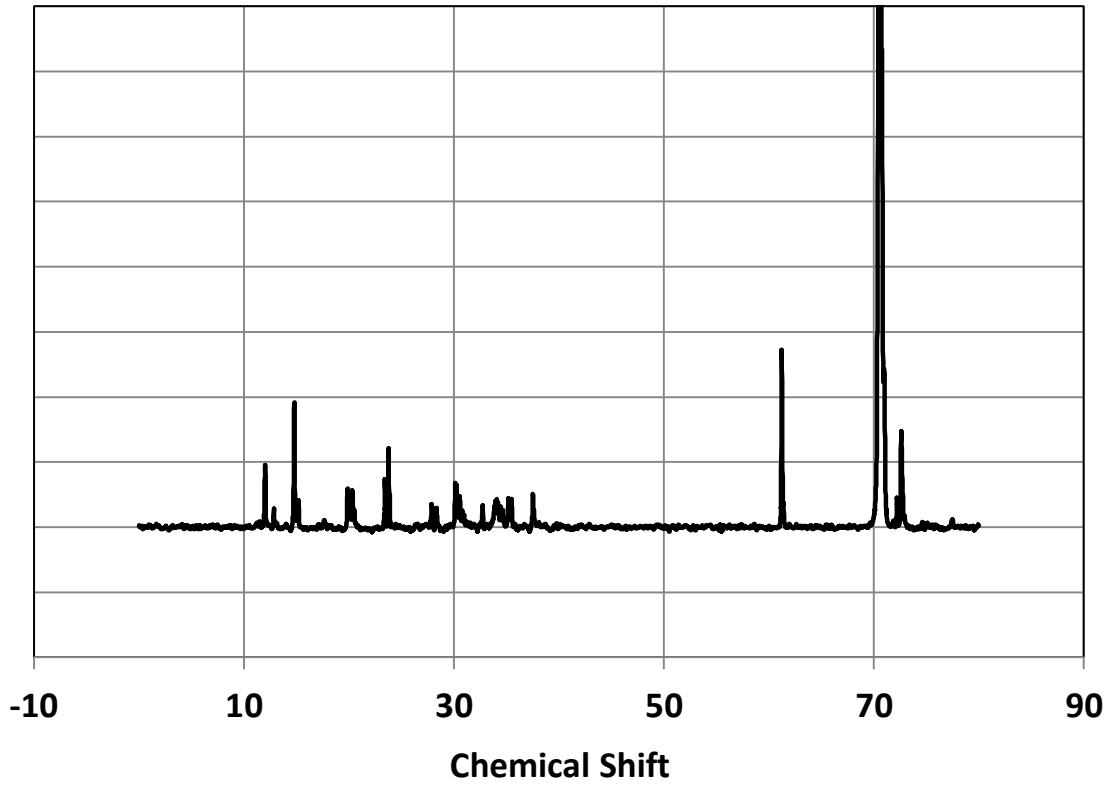


Figure 4-34 NMR-C results for Marlipal O13/120 before aging

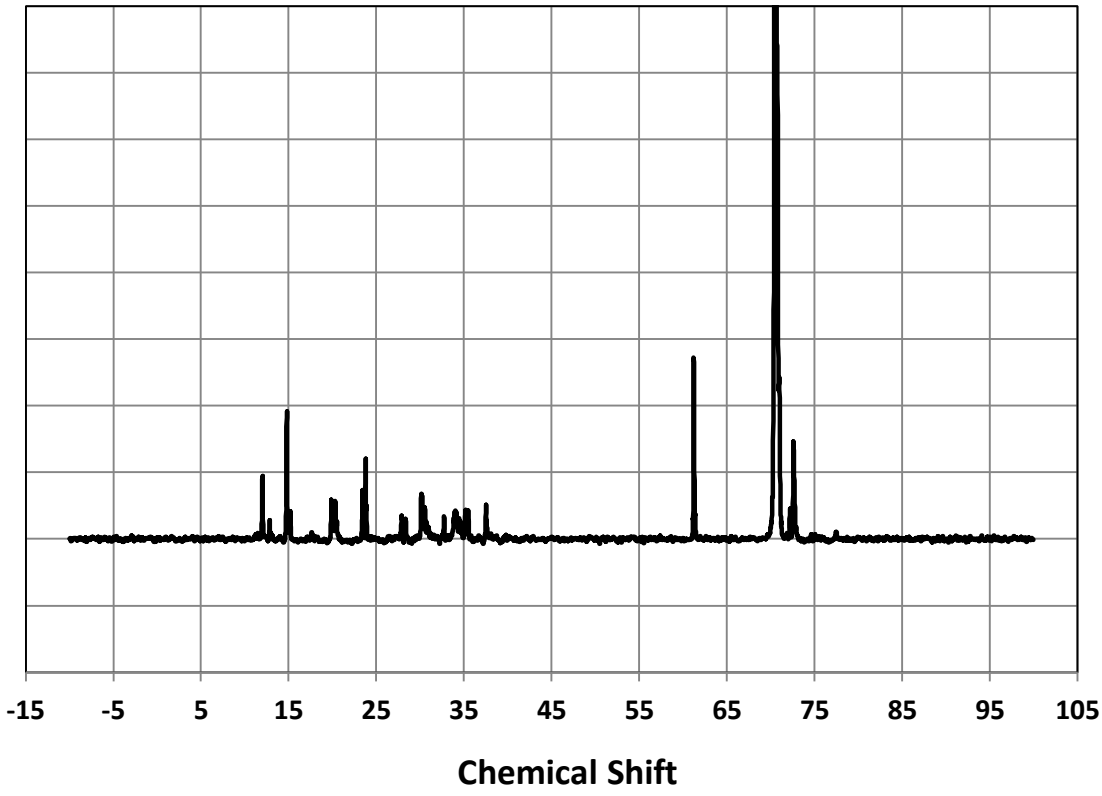


Figure 4-35 NMR-C results for Marlipal O13/120 after aging

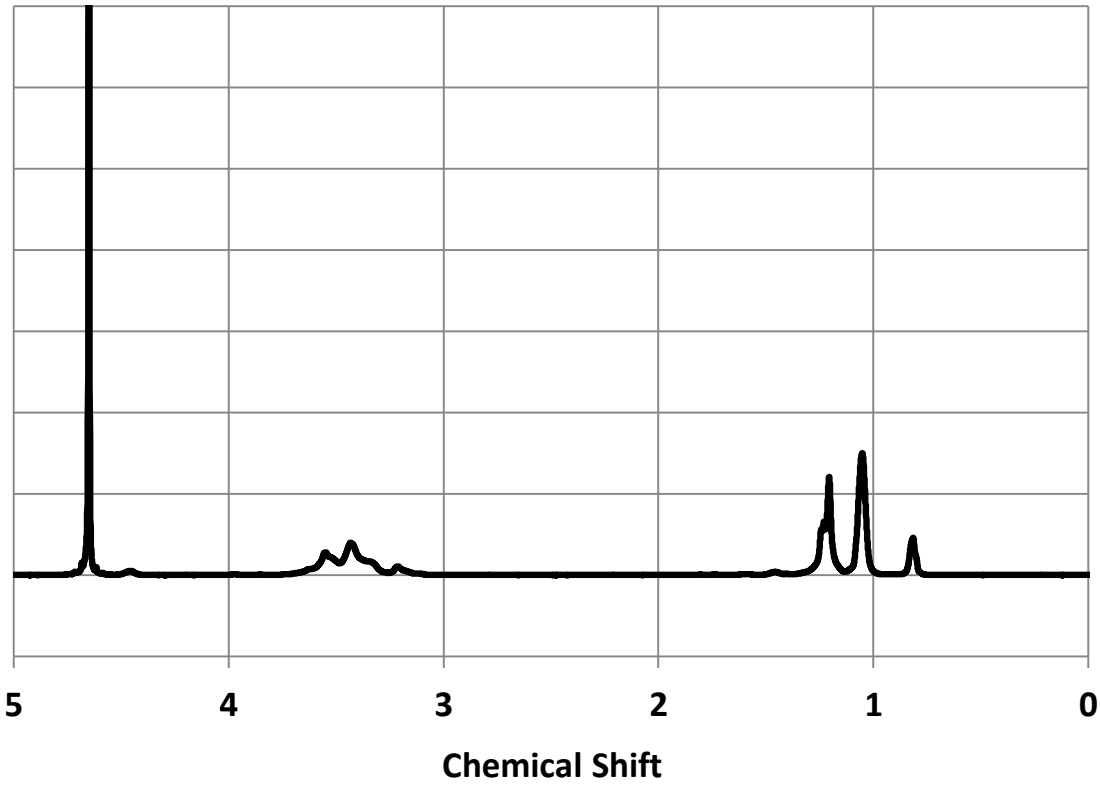


Figure 4-36 NMR-H results for Alfoterra 123-8s before aging

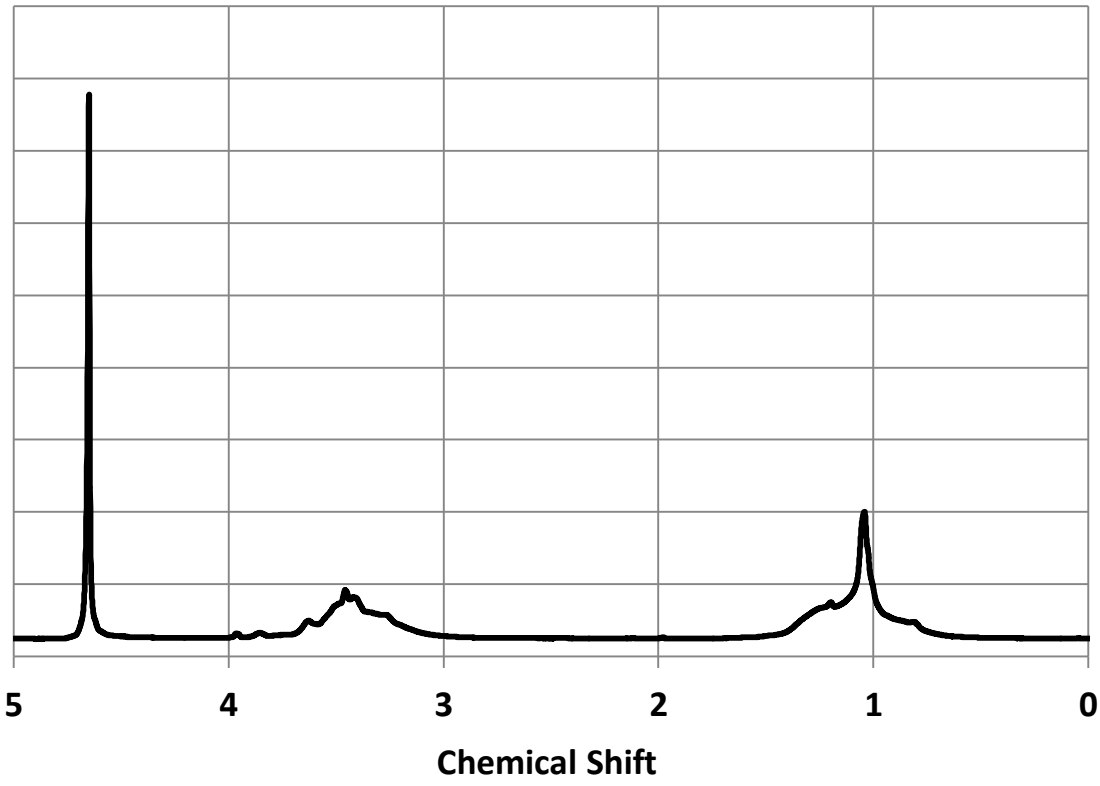


Figure 4-37 NMR-H results for Alfoterra 123-8s after aging

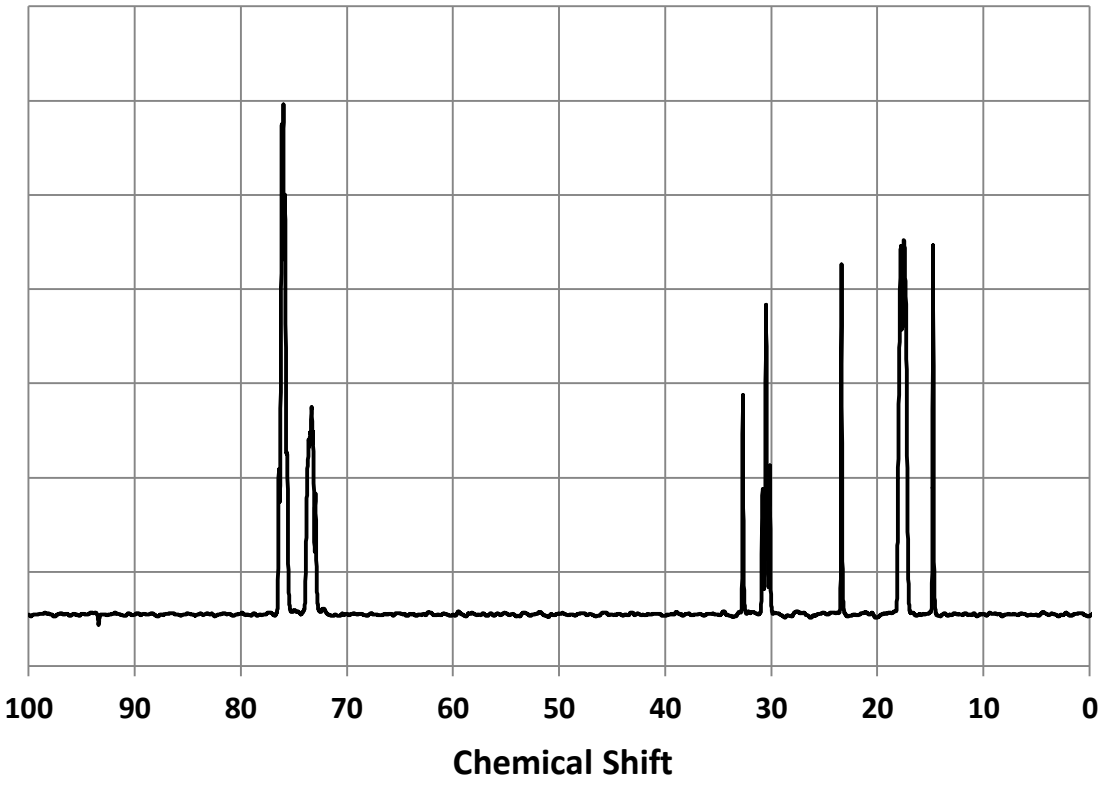


Figure 4-38 NMR-C results for Alfoterra 123-8s before aging

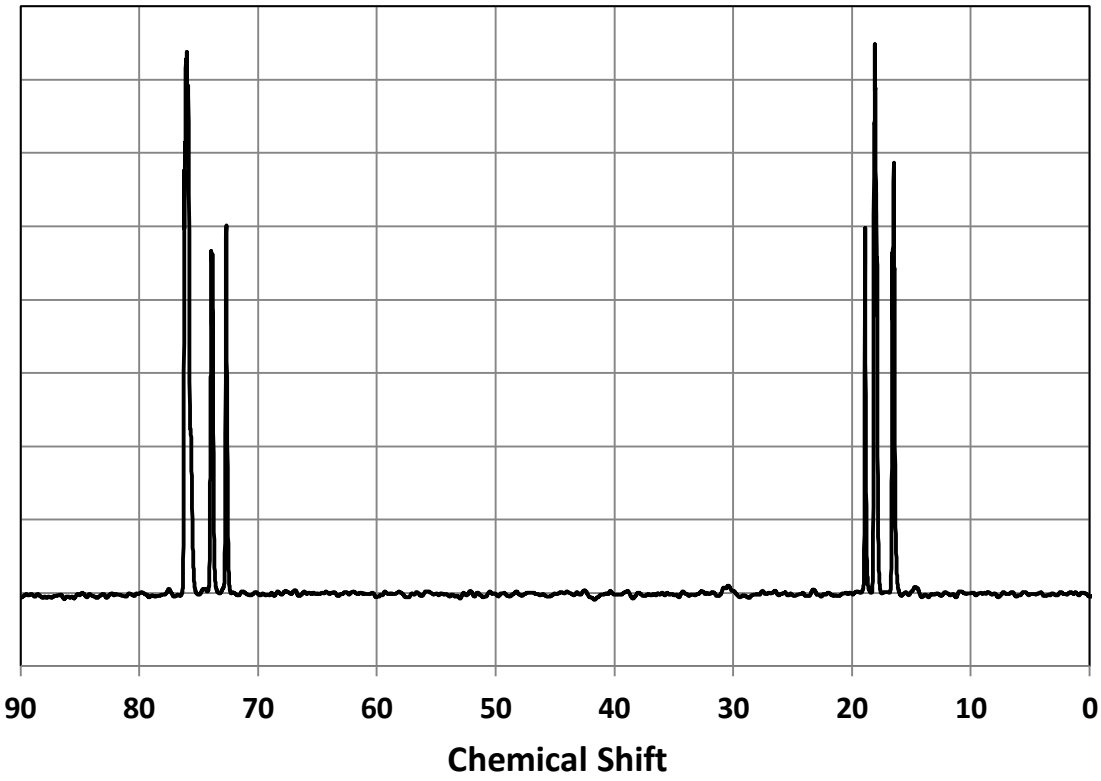


Figure 4-39 NMR-C results for Alfoterra 123-8s after aging

4.5: Inter Facial Tension (IFT) Results:

The surfactants are used in EOR to lower the interfacial tension between the oil and water. The surfactants increase the sweep efficiency by reducing the capillary number. A great deal depends on the type whether they are oil wet, water wet or mixed wet. Contact angle experiments can explain the nature of the rock. After analyzing results from different experiments and determining the optimum composition to be used, core flood experiments will be performed. Composition of the sample depends on concentration of the surfactants. The IFT experiments were performed to find out the optimum concentration of the surfactant where it has the minimum IFT values and remains stable at high and low temperatures.

System – 1:

Marlipal O13/120:

First experiment performed was to compare the IFT values between DIW and brine. Figure 4-40 shows the comparison between DIW and brine at different temperatures. The IFT value was very high for DIW which was 14.7mN/m at 40^{o}C. A decrease in the IFT value was observed as the temperature was increased and the minimum IFT value was achieved at 75^{o}C was 9.4mN/m. Increase in the temperature caused 37% decrease in the IFT values. DIW is not used for EOR in the field and brine is used instead. When the IFT was measured between brine and oil, 53% decrease in the IFT was observed. The increase in the temperature had no major effect on the IFT values in case of brine. Salts diffuse to the interface between oil and brine. Brine was preferred to be used in the field

instead as it gave low IFT values but still ultra-low IFT values were required for EOR applications which could be achieved using the surfactants.

Solutions with three different concentrations of the surfactant (0.1%, 0.2% and 0.3%) were prepared. Figure 4-41 shows the result as IFT versus temperature for different concentrations. For all three concentrations, the IFT values were observed to be almost the same at all temperatures. No major change was observed with changing the concentration. IFT value was the highest at room temperature which was 1.6mN/m and with the increase in temperature, 73% decrease was observed at 75^{o}C. The standard deviation was calculated at each temperature and the maximum value was found to be 0.08. This clearly indicates that from low to high temperatures, the IFT values were in the same range for Marlipal and no major change was observed when the concentration was changed. Marlipal surfactants were not tested in the past for IFT experiments and usually the decrease in IFT values was observed with increase in the concentrations of the surfactant. Talyor & Hisham (1995) reported the decrease in IFT values for non-ionic surfactants when the concentration of the surfactants was increased. The decrease in IFT value as compared with SW and DI water was 77% and 89% respectively at low temperatures. This decrease changed to 95% and 96% at higher temperatures which clearly indicated the impact of this surfactant. At higher temperatures, the surface activity of the surfactant increased and the surfactant was able to reduce IFT values.

Three different grades of Marlipal having different number of ethoxy groups were received. To investigate the effect of ethoxy groups on the IFT, solutions with the same concentrations for all three of them were prepared in the sea water. Marlipal 79, 99 and 120 had 7, 9 and 12 ethoxy groups, respectively. When the same experiment was

performed for three different solutions, the solution with the least number of ethoxy groups was observed to give the lowest IFT. 31% decrease in the IFT was observed when the number of ethoxy groups was decreased from 12 to 9 and a total of 60% decrease in the IFT was observed for 7 number of ethoxy groups. The decrease in IFT was proportional to the number of ethoxy groups as shown in Figure 4-42. The surface activity of the surfactant decreased with the increase in the number of ethoxy groups and Marlipal 79 was able to give the lowest IFT in this case.

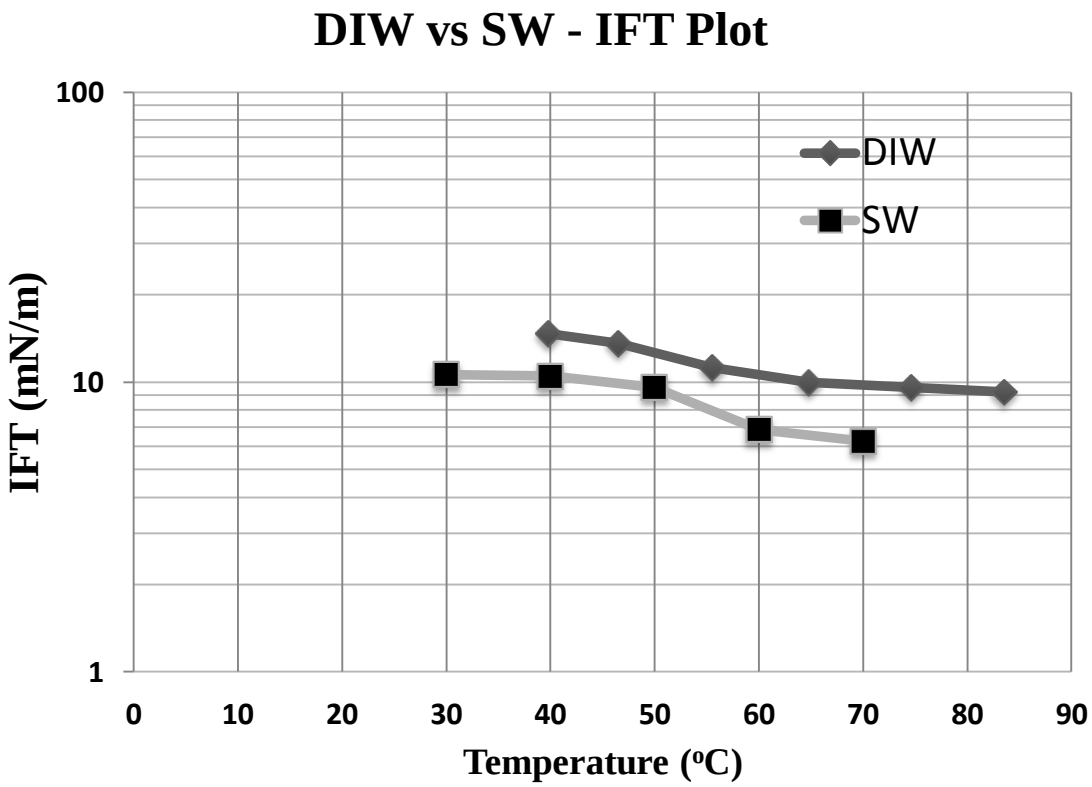


Figure 4-40 IFT vs Temperature for DIW and SW

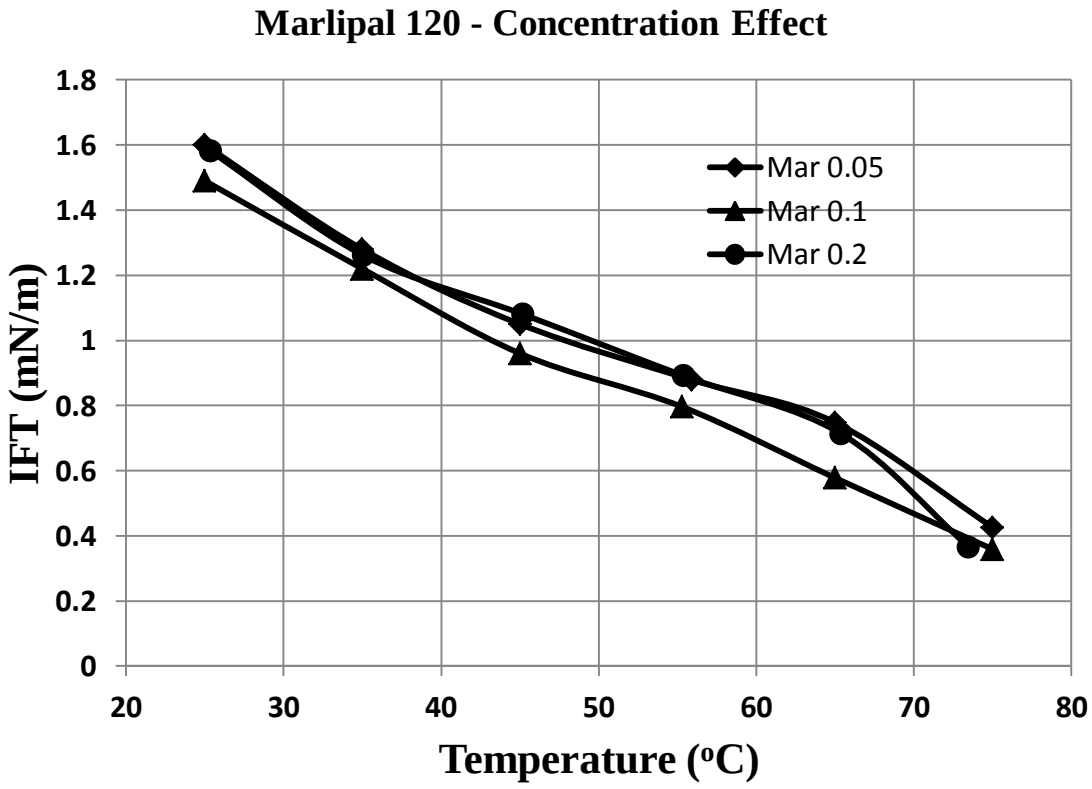


Figure 4-41 Effect of Marlipal O13/120 concentration on IFT in SW

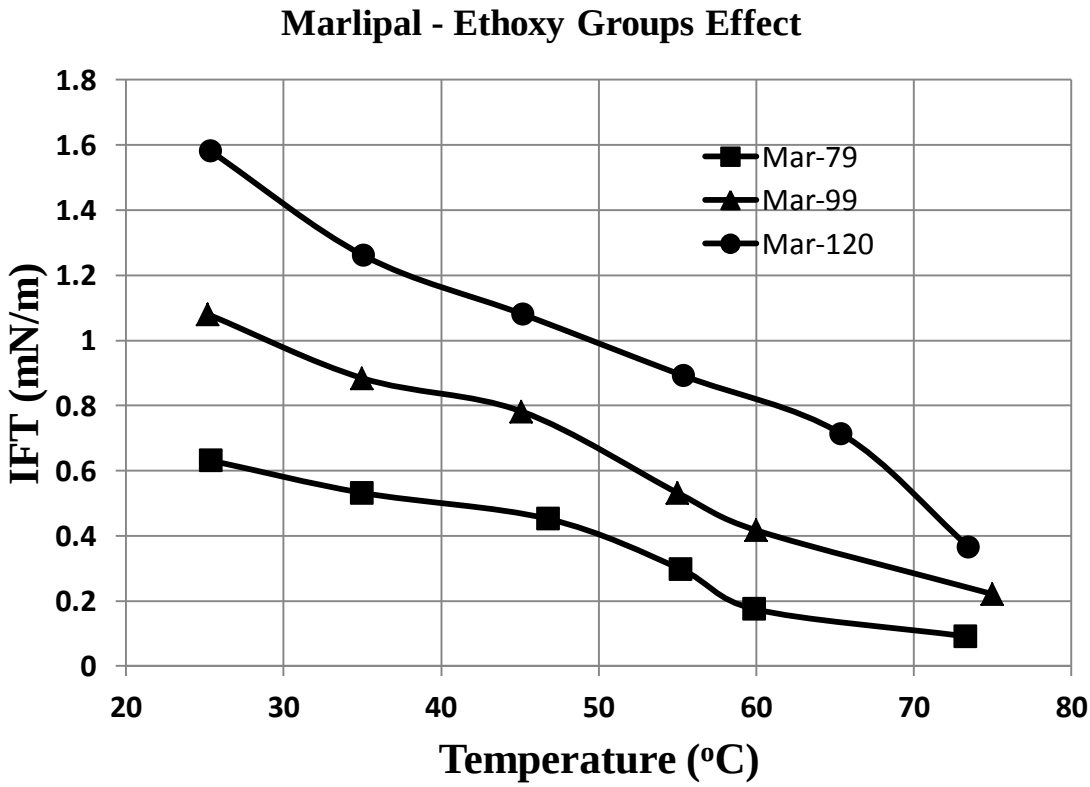


Figure 4-42 Effect of number of ethoxy groups on IFT in SW

System – 2:

Alfoterra 123-8s:

From the literature, it was clear that this class of surfactant lowers the IFT values up to the required level and thus works well with the sea water. Wu & Shuler (2005) worked with different grades of Alfoterra and reported ultra-low IFT results.

First step was to find out the optimum concentration of Alfoterra that could be used for further experiments. For this purpose, the solutions in DI water were prepared using four different concentrations.

0.1%, 0.2%, 0.25%, 0.3%, 0.35%, 0.4% 0.5% and 0.7% surfactant concentrations were used to find the optimum concentration. Temperature ramp experiment was performed to measure the IFT while increasing the temperature. Figure 4-43 shows the IFT values for all seven concentrations at room temperature. It was observed that as the concentration is increased, the minimum IFT was achieved at 0.3% which was 3.64mN/m and after this concentration, the IFT started increasing. The solution was tested up to 0.7% concentration and the IFT values were higher for all of these concentrations. Thus to achieve the lowest IFT, 0.3% concentration was selected. 0.3% was considered to be the CMC value for this grade of Alfoterra. Gupta (2008) also reported some CMC values for different grades of Alfoterra and the IFT either increased or remained constant after CMC value. Figure 4-44 shows temperature ramp experiment for the IFT values for four major concentrations of the surfactant and 0.3% was the optimum concentration giving the lowest IFT values at all temperatures. Further experiments were performed using 0.3% concentration for Alfoterra.

When Alfoterra was added in DI water, a huge decrease was observed as compared to the DI water alone but it was not able to give ultra-low IFT values. Alfoterra was added in sea water in the next step as salts had a major effect on this surfactant. With DIW, Alfoterra provided 3.64mN/m as the minimum IFT value. The IFT value decreased by 98% for low salinity and decreased up to 99.8% for high salinity giving 0.073mN/m and 0.00642mN/m for low and high salinity respectively. Salinity was varied to see the effect of salts on the IFT in the presence of Alfoterra. With sea water, IFT values increased with temperature. Alfoterra in DIW system showed a decrease in the IFT with increase in the temperature. In the first experiment, 14,000ppm salinity was used and it showed a decrease in the IFT values with the increase in temperature up to 45^{o}C and then IFT started to increase. This was possibly due to the surface activity of salts on the oil solution interface making it more stable at higher temperatures. Next experiment was performed with 28000 ppm salinity and same trend was observed except that the IFT values decreased up to 35^{o}C and then started to increase. Even after the increase, the IFT values were much lower as compared to any other experiment performed. Last experiment was performed using sea water with 57000 ppm salinity. Figure 4-45 shows all these different trends along with the DIW. Thus it was concluded that the IFT values are lowered to the required level. With the salinity and with the increase in temperature, this oil-surfactant solution becomes more stable giving high IFT values. Alfoterra was designed to deal with high salinity but at lower temperature. Seethepalli (2004) also reported decrease in the IFT value as salinity was increased for Alfoterra class of surfactants at room temperature. These experiments confirmed that the lowest IFT values

were achieved at low temperatures. The effect of the surfactant was more pronounced at low temperatures as Alfoterra was not designed for higher temperatures.

Co-surfactants are used in EOR to combine the properties of the two surfactants so that one may overcome the shortcomings of the other surfactant. From the previous experiments, it was observed that Marlipal had no optimum concentration to be used and all concentrations had almost the same effect in the experiments. The optimum concentration for Alfoterra was found out to be 0.3%. The solutions were prepared with different concentrations of Marlipal and 0.3% Alfoterra. Concentration of the Marlipal used was 0.1%, 0.2% and 0.3%. Figure 4-46 shows the results for all three concentrations as IFT versus temperature. The temperature ramp experiment was performed to observe the effect of the co-surfactant at high salinity and high temperatures. With 0.1% co-surfactant, results were almost the same as obtained without the co-surfactant. The IFT was increased with the increase in temperature with 0.1% concentration of the co-surfactant. But with 0.2%, Marlipal effect started dominating and the IFT values started to increase due to the co-surfactant which had higher IFT. The solution had the combined effect of both the surfactants. The major exception observed was the change in the trend of IFT values with the increase in temperature. For this solution, the IFT decreased with the increase in temperature because of the co-surfactant which was dominating in this composition. Marlipal was a thermally stable surfactant and showed no effect with the sea water while Alfoterra was not stable at high temperatures. Third experiment was performed with even higher concentration which was 0.3% of the co-surfactant. The IFT values were higher for this composition but the trend was similar to last experiment. This indicated that 0.2% was the optimum concentration of the co-surfactant. When higher

concentration was used than this optimum value, only the IFT values were increased but the same trend was observed. Thus for high temperatures and salinities, Alfoterra with a co-surfactant (Marlipal) was a better option with optimum concentrations

From the IFT experiments main results concluded were that Marlipal was not able to give ultra-low IFT but Alfoterra produced promising results in giving ultra-low IFT results with high salinity. For high temperature applications Alfoterra produced good results when used in combination with the co-surfactant which in this case was Marlipal.

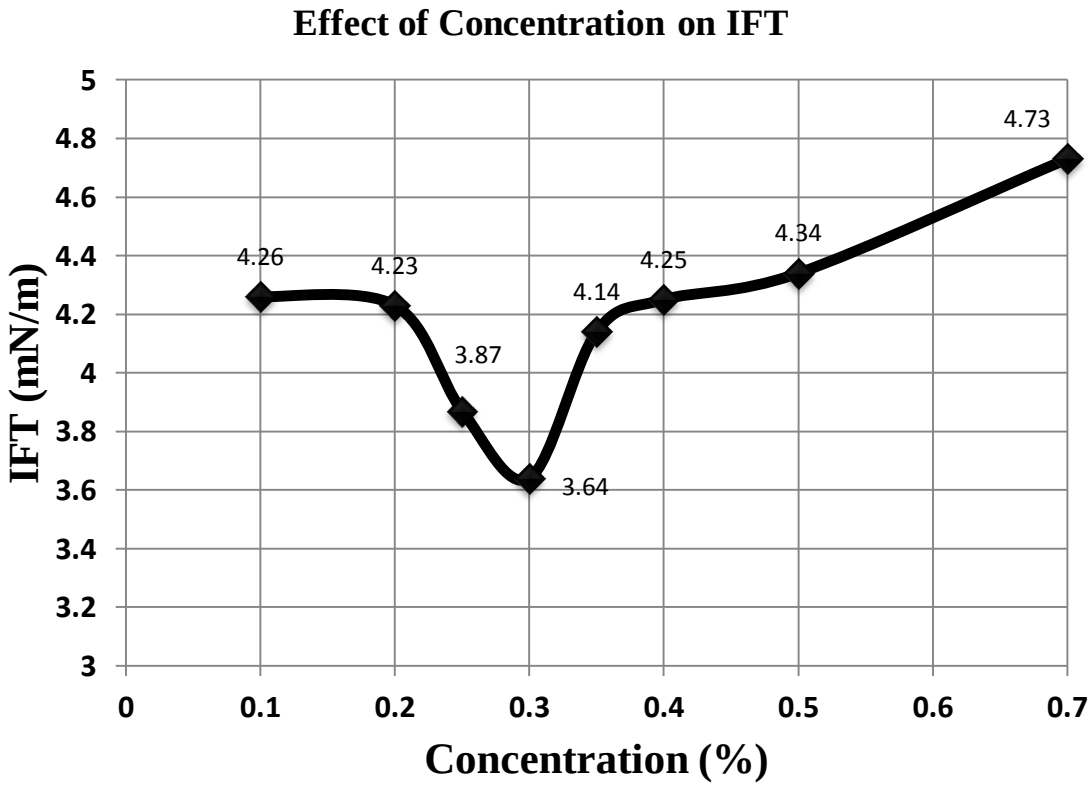


Figure 4-43 Effect of Alfoterra 123-8s concentration on IFT in DIW

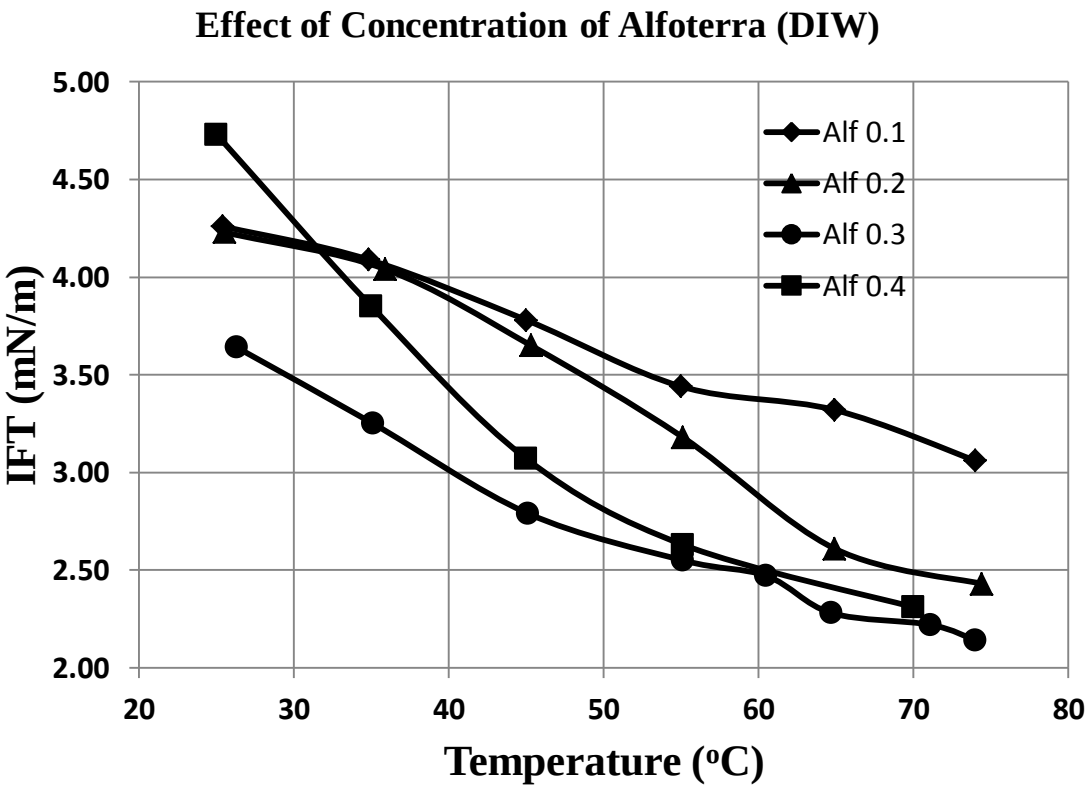


Figure 4-44 Effect of Alfoterra 123-8s concentration on IFT in DIW

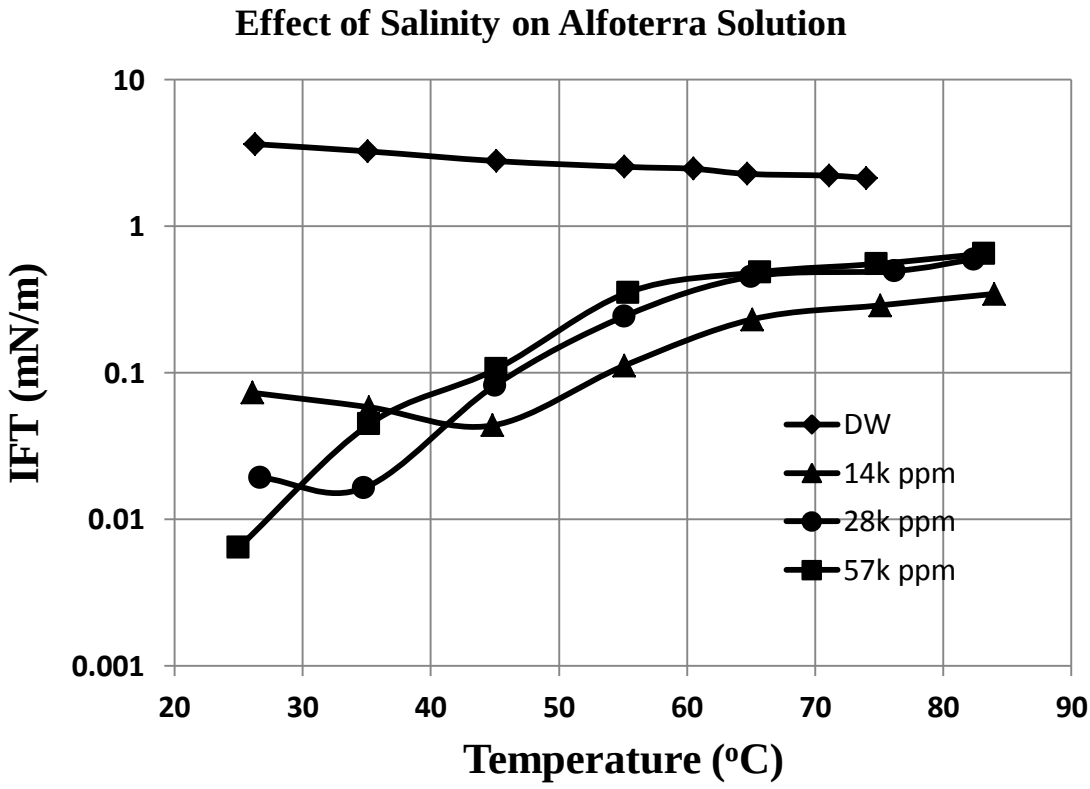


Figure 4-45 Effects of salts on the IFT of Alfoterra 123-8s solution

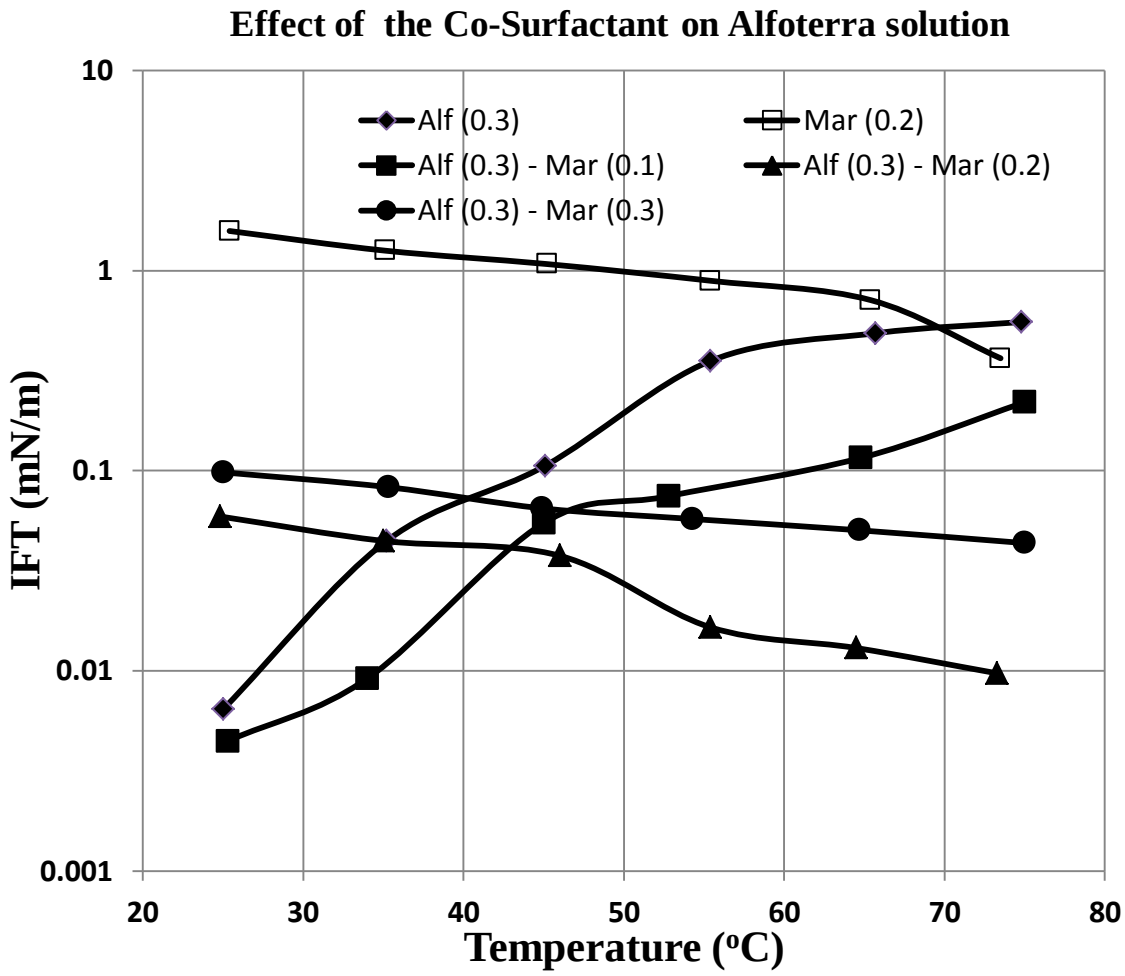


Figure 4-46 Effect of the co-surfactant on the IFT of Alfoterra 123-8s solution

4.6: Adsorption:

The surfactant loss due to adsorption during EOR is an important factor in selecting a specific surfactant. The surfactants are expensive and their adsorption in reservoirs can possibly increase the cost of oil extraction. EOR was introduced after ever-increasing cost of oil relative to the chemicals which were in the past not used as it adds to the cost in extracting a small amount of oil. With the passage of time, the increasing demands of oil and the availability of cost-effective chemicals in the market increased the oil recovery one stage up just by using the small amounts of chemicals. If the chemicals get adsorbed on the surface of rocks, it will take cEOR out of the competition again compared to the other techniques available in the market. Surfactants are thus screened out after studying their adsorption behavior. Sea water is also more useful than DIW due to the presence of salts which can decrease the IFT between the solution and the oil. Static adsorption tests were performed to investigate the adsorption of salts and the surfactant on carbonate reservoirs. For this purpose, precipitated calcium carbonate (PCC) was used in powder form to increase the surface area and to open maximum chances for the chemicals to get adsorbed. If the chemicals are able to give good results during these tests, it could be concluded that these chemicals perform much better when applied in the field. Ion Chromatography (IC) technique was used to measure the concentration of ions before and after adsorption. Ions are present in massive concentrations as sea water was used for the adsorption tests and IC was not capable of finding high ions concentration. Thus, samples were diluted which also produced dilution error in some measurements. As sodium chloride was the major salt in sea water so after dilution, sodium and chloride results were not accurate and reliable for the same sample.

Magnesium, calcium and sulfate provided much better results and thus only these three salts are discussed in the analysis. Four samples were prepared for sea water with and without oil at two different temperatures. Similarly, four samples were prepared for each surfactant to compare the adsorption results in the presence of the surfactants and also the adsorption of the surfactant itself. Figure 4-47 and Figure 4-48 show the cations and anions densities in the samples for each surfactant. Static adsorption tests took 48 hours to achieve equilibrium. The reference used was the concentration of ion in sea water before adsorption. Positive difference shows the adsorption of salts on PCC and negative difference shows the desorption of ions from PCC or the surfactant in the solution.

4.6.1 Calcium Adsorption:

PCC contains both the calcium and carbonate ions and sea water contains also calcium ions so there is a possibility of calcium absorption and desorption during the tests. The overall calcium density was measured. Figure 4-47 shows the results of Marlipal adsorption density for all samples. Sample 1 (SW+PCC 25^{o}C) and sample 2 (SW+Mar+PCC 25^{o}C) both indicated that the calcium was desorbed. Calcium desorbed more in the absence of the surfactant but desorption decreased in the presence of the surfactant. In sample 3 (SW+Oil+PCC 25^{o}C), desorption of the calcium was decreased. Sample 4 (SW+Mar+OIL+PCC 25^{o}C) showed little increase in desorption of calcium. Sample 5 ((SW+PCC 90^{o}C) and sample 6 (SW+Mar+PCC 90^{o}C) followed the same trend but at higher temperature. In sample 6, in the presence of the surfactant at higher temperature, desorption was little less as compared to the sample 5. At higher temperature, the oil effect decreased and sample 7 (SW+Oil+PCC 90 ^{o}C) showed more

desorption of calcium than at room temperature. Sample 8 (SW+Mar+Oil+PCC 90 ^{o}C) showed no effect of the surfactant on calcium ion.

Figure 4-48 shows the adsorption results for Alfoterra surfactant. This surfactant was similar to Marlipal in behavior. A figure 4-48 show that desorption of calcium was reduced in sample 2 (SW+Alf+PCC 25 ^{o}C) due to the presence of the surfactant and the resisting desorption of calcium. In the presence of oil, desorption was reduced even more (Sample 4 (SW+Alf+Oil+PCC 25 ^{o}C)). At higher temperature, the desorption increased due to more ion exchange between brine and PCC and it continued even in the presence of oil. Sample 6(SW+Alf+PCC 90 ^{o}C) and sample 8 (SW+Alf+Oil+PCC 90 ^{o}C) showed more desorption of calcium at higher temperatures than at room temperature.

4.6.2 Magnesium Adsorption:

Magnesium was present only in brine and it could only be adsorbed on PCC. Only possibility was that it replaced calcium and made a bond with carbonate as it has more affinity towards carbonate than calcium. For Marlipal, in Figure 4-47, magnesium showed adsorption for sample 1 and this adsorption increased in the presence of the surfactant in sample 2. In the presence of oil in sample 3, magnesium indicated no role in adsorption but in the presence of the surfactant, adsorption increased and was similar to sample 2. At higher temperatures, with the increasing desorption of calcium, adsorption of magnesium also increased. In sample 5, magnesium adsorption was the highest among all the samples and there was no oil and surfactant. When the surfactant was introduced, adsorption of magnesium decreased but it was still higher than the previous samples. In the presence of oil at higher temperature, adsorption decreased as shown in sample 7 of

Figure 4-47. With the introduction of the surfactant, magnesium adsorption remained unaffected with the presence of oil and it showed the similar behavior as without oil.

Figure 4-48 shows the adsorption results for Alfoterra. Alfoterra samples followed almost the same trend as for the Marlipal. Magnesium adsorption increased in the presence of the surfactant at low temperatures. Oil influenced and decreased the adsorption but with the surfactant in the sample, oil effect was reduced and magnesium showed more adsorption. At higher temperatures, adsorption increased again and in the presence of the surfactant, it decreased by little margin. In the presence of the surfactant, oil had no effect on the adsorption and it showed behavior similar to the previous surfactant.

4.6.3 Sulfate Adsorption:

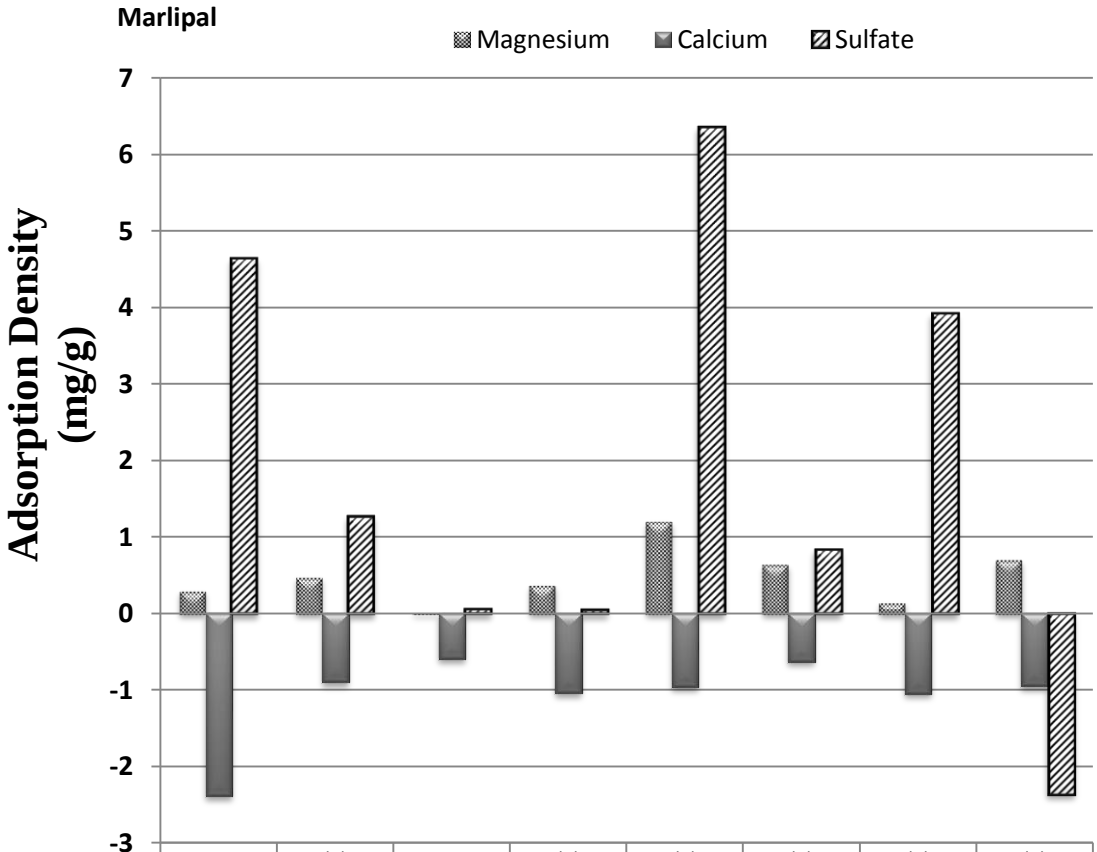
Sulfate was present in the brine but it had more affinity towards calcium and magnesium than carbonate so there was a possibility that it would get adsorbed on PCC. Also, both the surfactants had sulfate at the end of the chain and this sulfate was also expected to play some role in the adsorption.

Figure 4-47 shows the results for sulfate adsorption with Marlipal. Sample 1 showed great adsorption of sulfate on PCC but when Marlipal was introduced in sample 2, adsorption decreased up to 80%. Sulfate present in the Marlipal was easier to bet adsorbed on PCC than sulfate present in the brine so sulfate present in the brine was not much adsorbed. In the presence of oil, sulfate neither adsorbed nor desorbed and the change in density was negligible. At higher temperatures, sample 5 showed more adsorption but when Marlipal was added in sample 6, adsorption again reduced due to the possible reason of the presence of sulfate in the surfactant structure. In the presence of oil, sample 7 showed good adsorption and oil effect reduced at higher temperatures. In

sample 8, when Marlipal was introduced along with oil at higher temperature, sulfate showed desorption. As PCC does not contain sulfate and desorption was not expected, this could possibly due to sulfate present in the surfactant structure which could easily be separated from the surfactant at higher temperature. As the surfactant reduced adsorption at room temperature, it even produced sulfate ion at higher temperature.

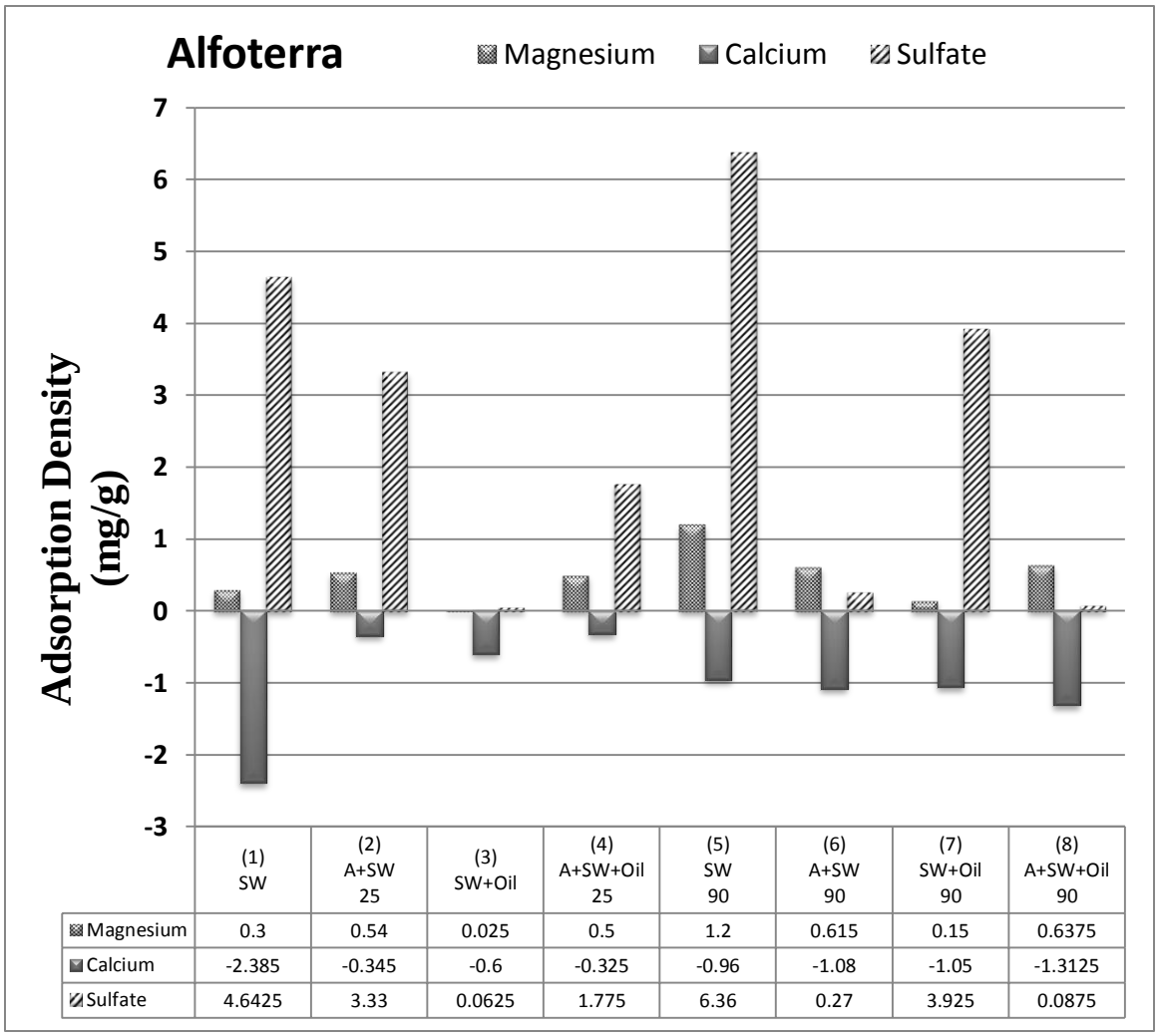
Figure 4-48 shows the adsorption results for sulfate in the presence of Alfoterra. It showed similar behavior because Alfoterra also had sulfate ion at the end of the chain. Similar behavior was observed and the adsorption of sulfate decreased in the presence of Alfoterra at room temperature. With the addition of oil, adsorption was minimized but with the presence of the surfactant, there was little adsorption. At higher temperatures again with the surfactant and oil, sulfate adsorption was high. When the surfactant was introduced, adsorption reduced up to 96% possibly due to the presence of sulfate ion in the surfactant. At higher temperature, oil again was not effective in reducing the adsorption of sulfate but the surfactant was more effective. It actually reduced the sulfate adsorption even at higher temperature.

From adsorption experiments major conclusion was that calcium was desorbed in all experiments. Magnesium was not adsorbed but sulfate ions were adsorbed on PCC as it has more affinity towards carbonate ions than calcium. Surfactants also contain sulfate ions and this made sulfate concentration overall high in the samples after adsorption.



	(1) SW	(2) M+SW 25	(3) SW+Oil	(4) M+SW+Oil 25	(5) SW 90	(6) M+SW 90	(7) SW+Oil 90	(8) M+SW+Oil 90
Magnesium	0.3	0.48	0.025	0.375	1.2	0.645	0.15	0.7
Calcium	-2.385	-0.9	-0.6	-1.0375	-0.96	-0.63	-1.05	-0.95
Sulfate	4.6425	1.275	0.0625	0.05	6.36	0.84	3.925	-2.35

Figure 4-47 Adsorption density for Calcium, Magnesium and Sulfate in presence of Marlipal O13/120



	(1) SW	(2) A+SW 25	(3) SW+Oil	(4) A+SW+Oil 25	(5) SW 90	(6) A+SW 90	(7) SW+Oil 90	(8) A+SW+Oil 90
Magnesium	0.3	0.54	0.025	0.5	1.2	0.615	0.15	0.6375
Calcium	-2.385	-0.345	-0.6	-0.325	-0.96	-1.08	-1.05	-1.3125
Sulfate	4.6425	3.33	0.0625	1.775	6.36	0.27	3.925	0.0875

Figure 4-48 Adsorption density for Calcium, Magnesium and sulfate in presence of Alfoterra 123-8s

4.7: Phase Behavior

Phase behavior experiments are performed to screen the surfactants. These experiments give extremely valuable insight information about the surfactants. These experiments were first introduced by Winsor who studied the micro-emulsions. Chemicals usually form three types of micro-emulsions. Different names have been used to define these emulsions and mostly adopted terms for these types are Type I, II and III. Type I micro-emulsion is also called Oil in Water (O/W Micro-emulsion). In this emulsion, oil droplets are surrounded by water molecules and excess oil is separated. Type II micro-emulsion, also called Water in Oil (W/O Micro-emulsion), contains water droplets surrounded by the oil molecules. The surfactant and excess water or brine gets settled at the bottom. Type III micro-emulsion is in between Type I and Type II emulsions. Excess oil gets separated at the top and excess brine gets settled at the bottom and amidst them oil, water and the surfactant molecules form a micro-emulsion. From the EOR point of view, Type III is the best emulsion as in this emulsion, the surfactant shows good interaction with the oil and brine. Before performing the IFT experiments, phase behavior experiments can explain which surfactants will give ultra-low IFT values. Some surfactants do not give low IFT but are still performing fine for oil recovery. To screen the surfactants, phase behavior plays an important role. Thus different setups were prepared to achieve different results. First of all, samples containing fixed salinity and varying concentrations of both the surfactants were prepared. Then the salinity was varied to find the optimal salinity which explains at which salinity this surfactant will perform best in the field and give ultra-low IFT values. Optimal salinity is usually used to find the IFT values. After initial screening, the best surfactants to give ultra-low IFT values are again tested and the IFT is

determined using conventional methods to compare the two results. The phase behavior experiment setup was designed accordingly. Caped tubes were used to perform the experiments. Equal volume was used for oil and brine and the initial interface for all the samples was kept fixed at 5ml as 5ml of oil and brine was used. These tubes were set on rotation for better mixing for 24 hours and then left to achieve the equilibrium. Some surfactants were expected to achieve equilibrium within 3 days while some take up to 21 days. In this case, the surfactants achieved equilibrium after 1 week and phases were separated.

In general, non-ionic surfactants are not expected to give any kind of micro-emulsion and these surfactants are used in combination with the other surfactants to give thermal stability. In this case, Marlipal 120 showed the same results. In the first experiment, concentration of NaOH was kept fixed at 1 M and the concentration of Marlipal was varied between 0%, 0.1%, 0.2%, 0.3%, 0.4% and 0.5%. After achieving equilibrium, no micro-emulsion was observed in any sample. As these are non-ionic surfactants and micro-emulsions are formed due to the presence of hydrophilic and hydrophobic groups at the head and tail of the surfactants. In these surfactants, the absence of charges at the ends of the chains did not allow to create any micro-emulsion, phases were separated and the interface was clear at 5 ml. Subsequently, the salinity scan was performed to make sure that there was no effect of salts on the surfactant. Six samples with salinity of 0, 10k, 20k, 30k, 40k and 50k ppm were prepared containing fixed 0.1% concentration of the surfactant. Again the results were quite obvious and the equilibrium was achieved quickly after the rotation was stopped. No micro-emulsion was observed for these experiments either. Again the reason was absence of any kind of charges in the surfactant

structure which could interact with the oil and produce any type of micro-emulsion. Same experiments were repeated at higher temperatures and same results were achieved. Interface was much clear at higher temperatures but no micro-emulsion was observed. Experimentation with this surfactant was continued to determine whether this surfactant would give any results in EOR or not. Final experiment of core flooding was performed to observe the role of this surfactant in EOR. From the phase behavior experiments, this surfactant was concluded not to give good results in oil recovery as it had no interaction with the oil.

On the other hand, when the same experiment was performed using Alfoterra, it performed extremely well. Six samples were prepared to optimize the concentration of the surfactant for producing the best emulsion. Concentrations used were 0%, 0.1%, 0.2%, 0.3%, 0.4% and 0.5%. As 0% concentration referred to brine only containing 1M NaOH, it formed Type II micro-emulsion and the whole tube was filled with oil. Low concentrations of Alfoterra didn't show much change and small amount of the surfactant was not enough to produce Type-III micro-emulsion. At 0.3% concentration, clear Type-III micro-emulsion was formed. Afterwards with higher concentrations, the micro-emulsion was not very clear. It was due to the excess charges present in the solution. Thus the interaction between the oil and the brine was the best at 0.3% Alfoterra. In the next experiment, salinity scan was performed. 0, 10k, 20k, 30k, 40k and 50k ppm of NaOH were used with six samples of Alfoterra whose concentration was kept fixed at 0.3% as obtained from the previous experiment. At low salinity, micro-emulsion was not clear but at 30k ppm clear Type-III micro-emulsion was observed. At higher salinities, micro-emulsion was observed but its length was very short. It was probably changing to

Type-II micro-emulsion as after Type-III micro-emulsions, the surfactants produce Type-II micro-emulsions at higher salinities. Figure 4-49 shows results from the first experiment for Alfoterra; micro-emulsion is visible with 0.3% Alfoterra. Salinity scan is shown in Figure 4-50. At 30k ppm salinity, clear Type-III micro-emulsion was observed. After getting micro-emulsion, the optimal salinity was found for each sample. As shown in the table, optimal salinity is the solubilization ratio of the surfactant and the oil. The value at which the volume of the two is equal is expected to give the lowest IFT value. Although in this experiment, volume of the oil and the surfactant in micro-emulsion was not the same but the optimal salinity was still found for each sample.

The next experiment was performed for the samples at higher temperatures. Alfoterra was not stable at higher temperatures and the expected results were obtained. No micro-emulsion was produced at higher temperatures. This was possibly due to the complete breakup of the surfactant structure at higher temperatures. Thus, no micro-emulsion was produced at higher temperatures but at low temperatures, Alfoterra produced good quality results.

Marlipal was not able to produce micro-emulsions but on the other hand Alfoterra produced micro-emulsions with 0.3% concentrations. Also salinity scan tests showed that optimum salinity for Alfoterra was 30,000ppm and it will give lowest IFT with 0.3% concentrations and 30,000ppm salinity.

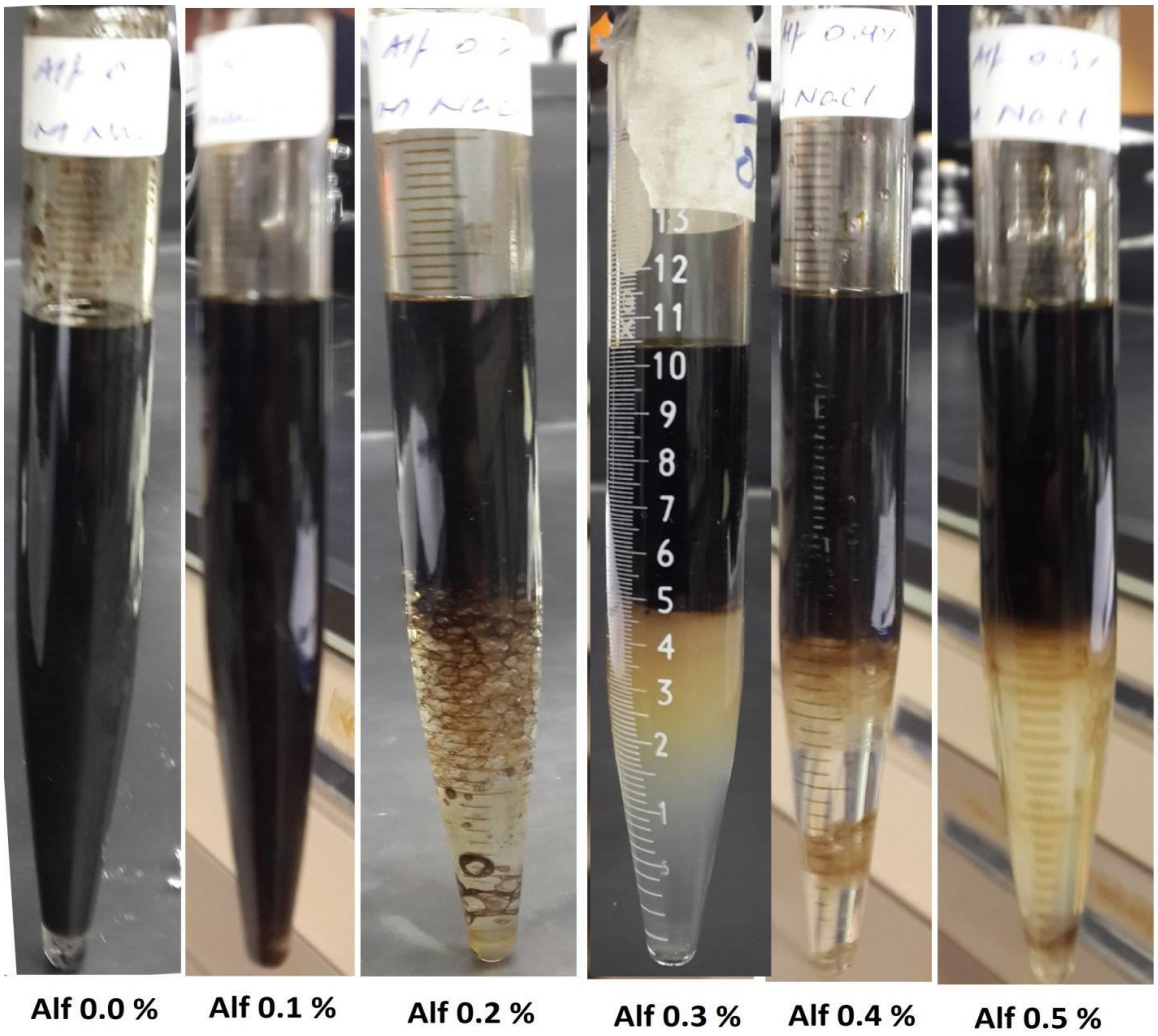


Figure 4-49 Phase behavior results for different Alfoterra 123-8s concentrations

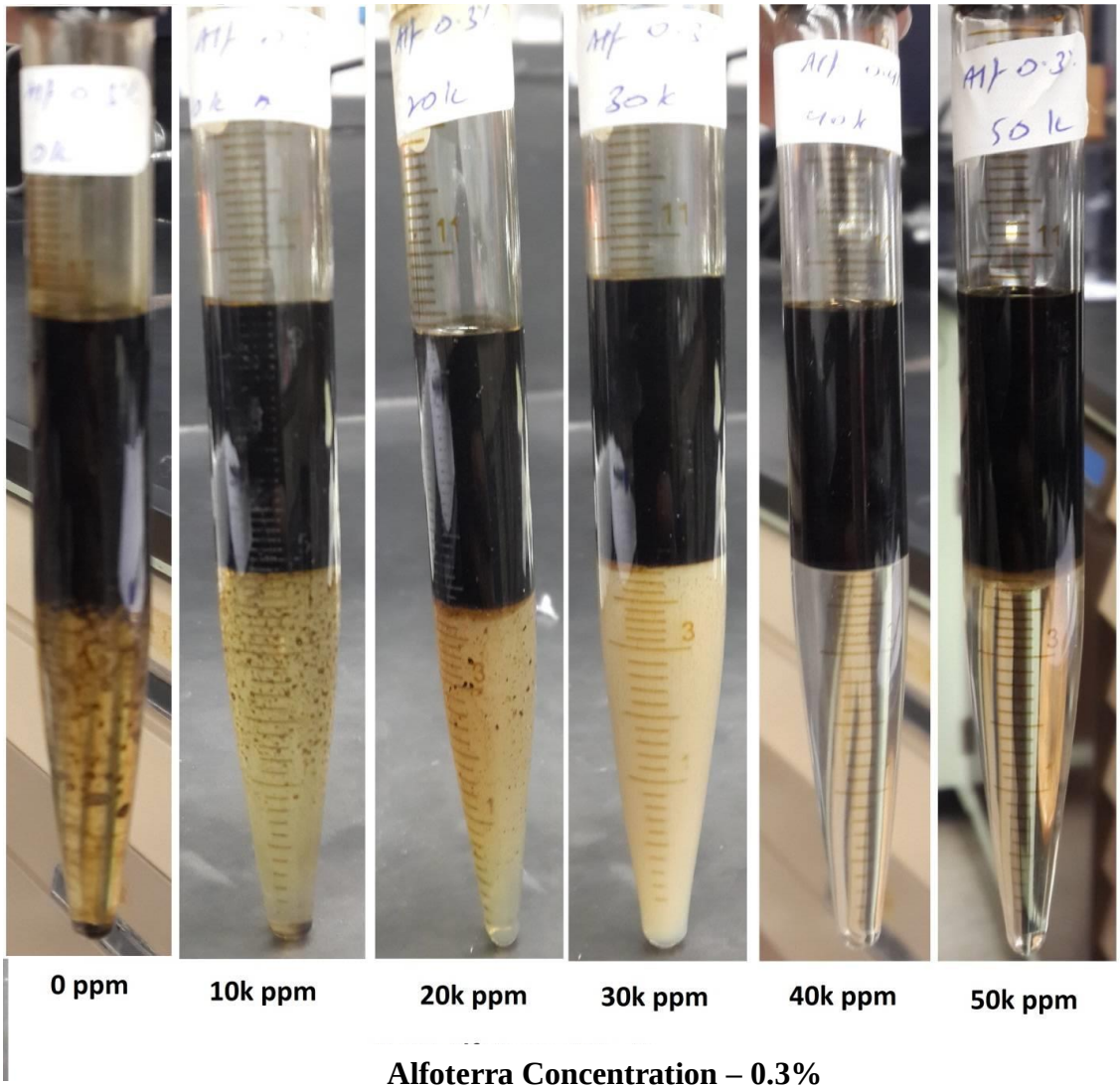


Figure 4-50 Effect of salts on phase behavior of Alfoterra 123-8s

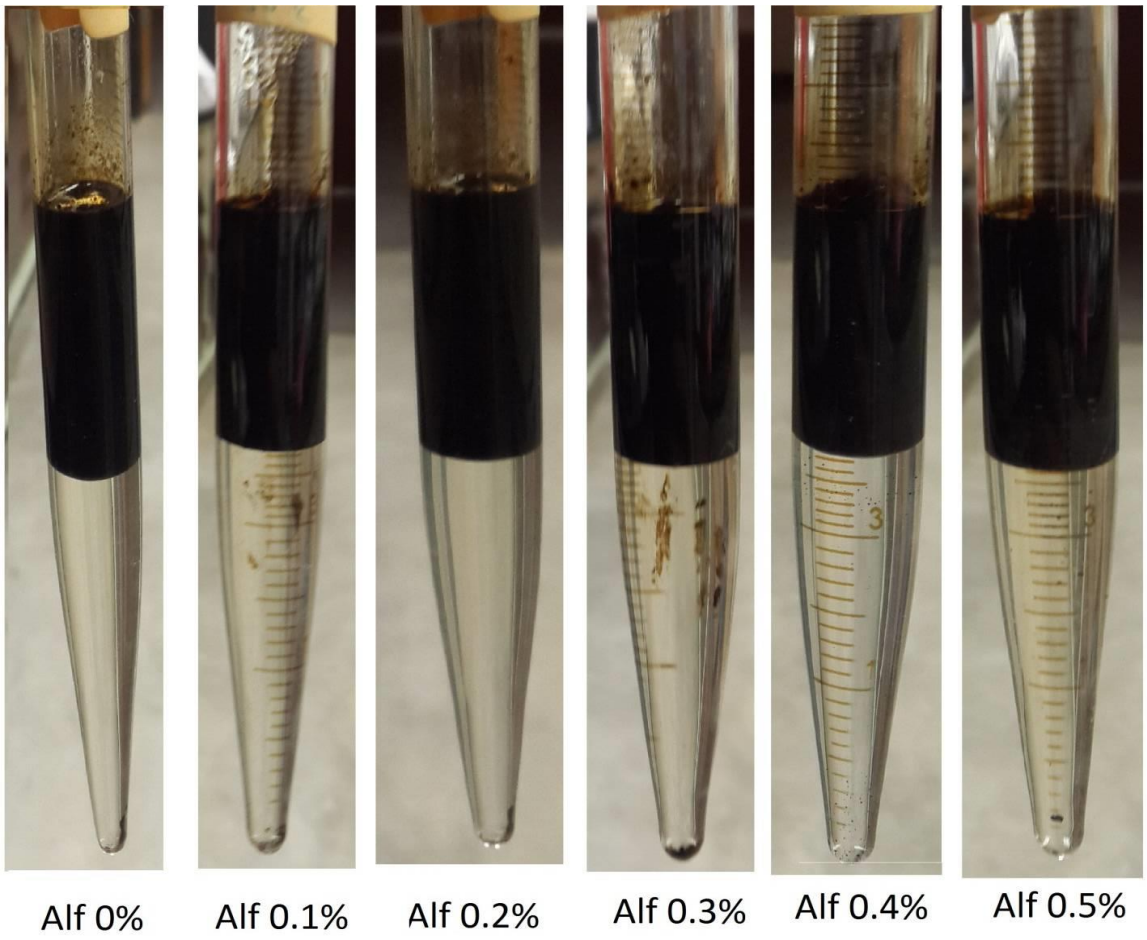
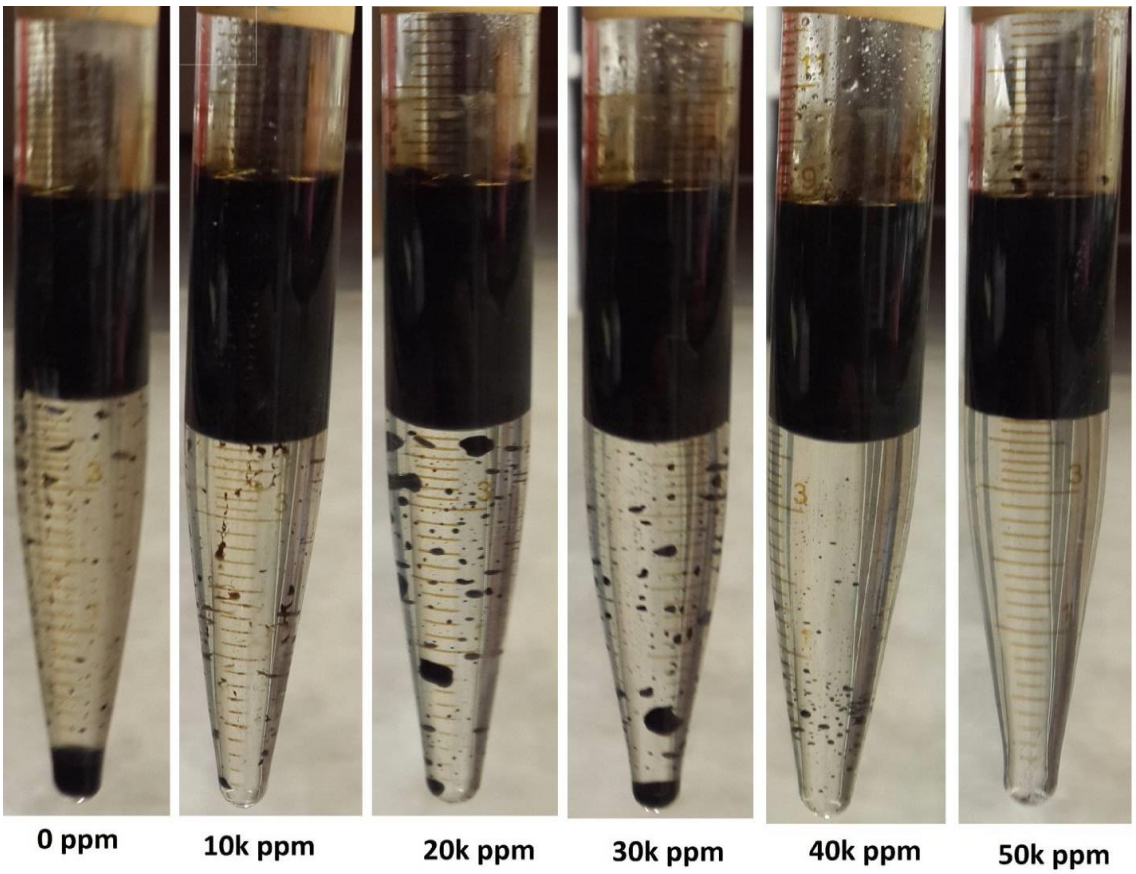


Figure 4-51 Phase behavior results for different Alfoterra 123-8s concentrations at 90°C



Alfoterra Concentration = 0.3%

Figure 4-52 Effect of salts on phase behavior of Alfoterra 123-8s at high temperature (90^{o}C)

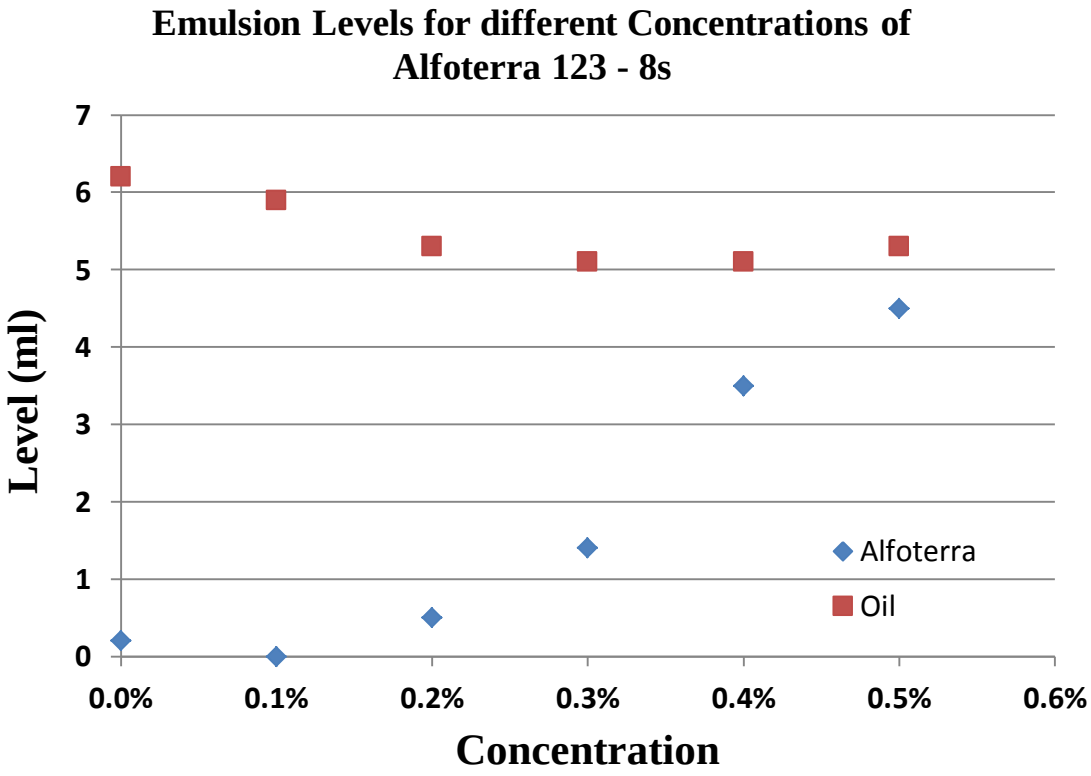


Figure 4-53 Salinity scan for phase behavior of Alfoterra 123-8s

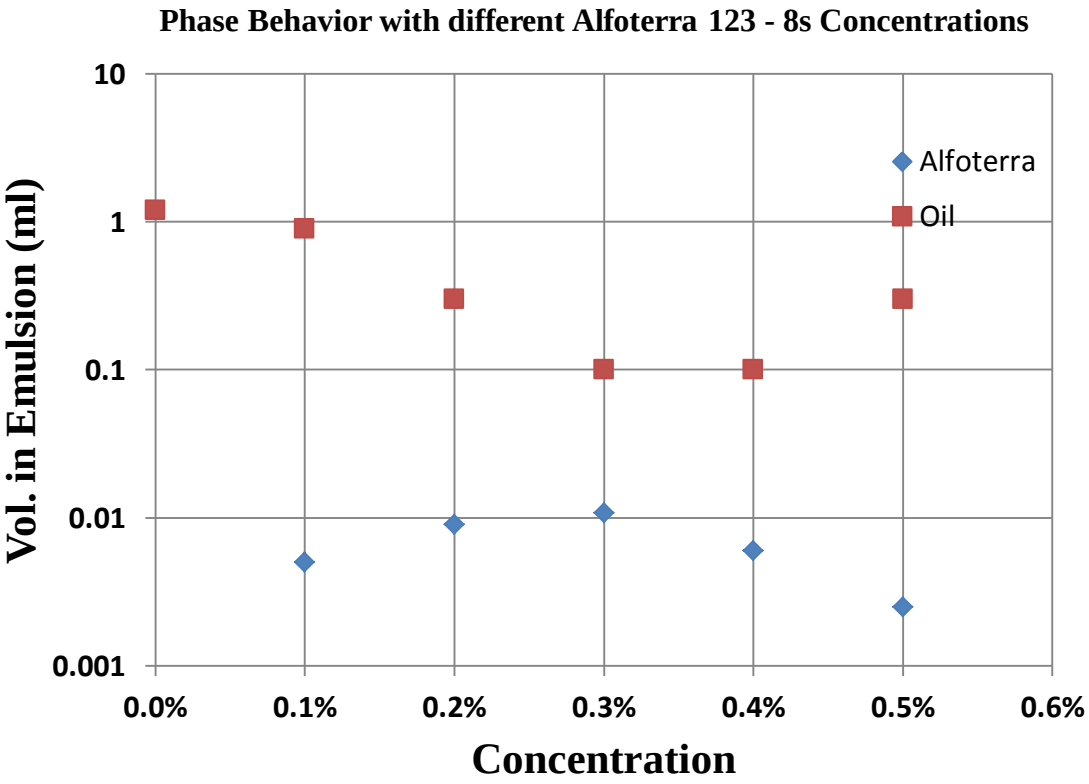


Figure 4-54 Effect of Alfoterra 123-8s concentration on phase behavior

4.8: CORE FLOODING

Core flooding experiments were performed to investigate the potential of SP-Solutions in cEOR. The cores used were Indiana Limestone. The cores were 12 in long and their diameter was 1.5 in. Pore volumes of cores were measured during their saturation with the formation water. First step was to saturate the cores with the formation water. Their weight was measured before and after the saturation. The difference of the two gave us the pore volume when divided with the density of the formation water (1.21 g/cm^3). After the saturation, the formation water was injected at different flow rates to measure the permeability using Darcy Law. The core was then saturated with oil and allowed to age for 15 days. After aging, the core was flooded with SP solutions. In this case, two experiments were performed for two different SP-systems. First experiment was performed for Alfoterra and HPAM whereas in the second experiment, Marlipal was used with HPAM.

4.8.1 Core Flood – 1:

Pore volume for the first core was 56.14 cc and the porosity was 0.1654. The permeability was measured using the formation water at different flow rates from Darcy Law for linear flow through porous medium. The flow rates used were 0.25, 0.5, 0.75 and 1 cc/min. Darcy Law gave us the permeability of the core which was 80 mD. It was calculated from the slope of the plot between pressure drop and flow rate as shown in Figure 4-55. After calculating the permeability, the core was flooded with oil at 0.5cc/min and the flow was continued till no more formation water produced. Flow direction was reversed several times to achieve the minimum S_{wi}. Initial Water Saturation was reduced from 100% to 36%. The permeability of the core was low which restricted to

maintain low flow rate as high flow rate could cause plugging in the core or damage the core. The temperature was maintained at 90^{o}C during aging and subsequently for the whole experiment. The confining pressure, which represents the pressure of the reservoir, was maintained at 2000 psi. The back pressure or Pore Pressure was build up to 500 psi. The back Pressure represents that pressure at which chemicals will be injected into the reservoir. As S_{wi} was 36%, volume of oil present in the core was 36 cc and flooding was carried out to recover maximum of this amount.

First step was to inject brine with salinity of 57000 ppm. In the literature, different results have been cited for different systems and for different conditions. Sriram (2012) reported some of the similar results for propoxylate surfactants. Brine was injected at the rate of 0.5cc/min. Oil started to come out as soon as brine injection was started. Maximum oil was recovered at 0.3 pore volume (PV) of brine injection. After that, traces of oil kept coming out but after 2.5 PV, no more oil was produced and brine injection was stopped at that point. The total oil recovered from brine was 42.47% and the volume recovered for each 0.1 PV was measured.

In the second step, SP-solution was injected. Concentration of HPAM was 0.25% and for Alfoterra, it was 0.3% as optimized from the IFT experiments. The flow rate for the SP solution was 0.75cc/min. With the polymer, sweep efficiency was increased and the surfactant reduced the IFT. Oil recovery was increased up to 71.28%. Oil recovery against each 0.1 PV of the SP-solution injected is shown in Table 4-1.

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The third step was to inject brine again and to produce any traces of oil possible. Brine was injected at 0.75 cc/min. Brine pushed the SP solution still present in the core and produced more oil. Thus oil recovery increased up to 81.44% with this third injection. All the three injections and oil recovery results are shown in Figure 4-56. Total 1.8 PV of SP-solution was used for 28% oil recovery increment.

The polymer played its role in increasing the viscosity and sweep efficiency of the solution and Alfoterra lowered the IFT. With the combination of both, excellent results were obtained and the recovery was almost twofold. Alfoterra was not thermally stable at higher temperatures but as already explained with the help of rheology and TGA that with the combination of the polymer and when exposed for a shorter period of time, Alfoterra could perform better. Thus, excellent results were obtained from the core flood experiment. Combination of the polymer and the surfactant proved to be successful regarding core flood and still the concentrations of both were very small and showed excellent potential for EOR.

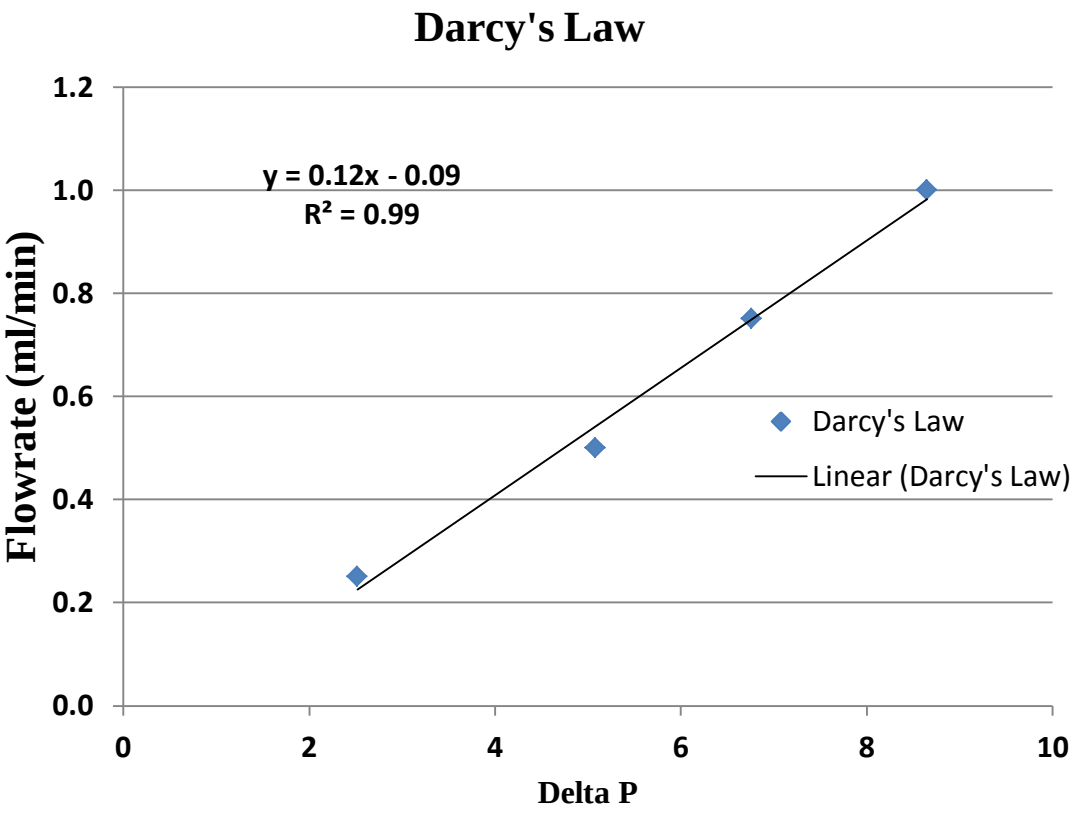

Figure 4-55 Formation water flow rate vs pressure drop for permeability calculations in Core Flood - 1

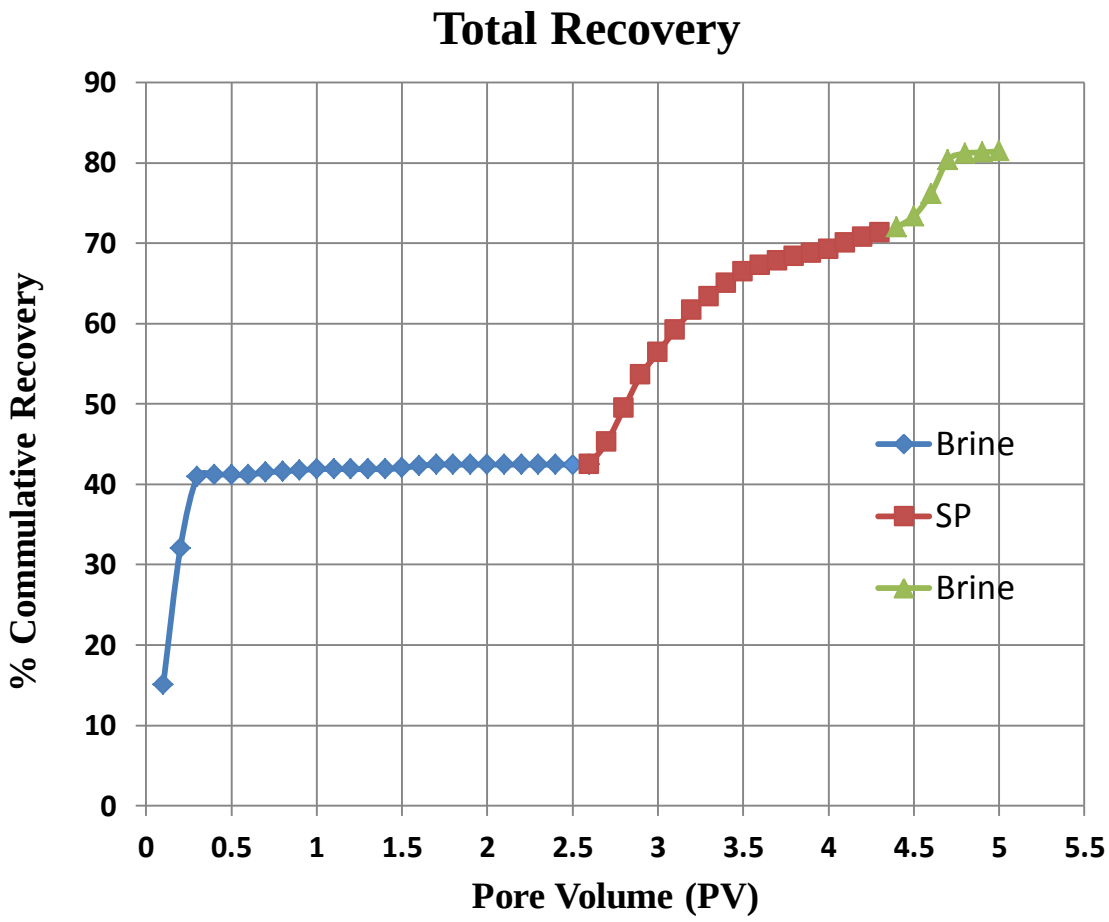

Figure 4-56 % recovery after brine and SP Flooding in Core Flood - 1

Table 4-1 Oil recovery % for different pore volume injections of SP in Core Flood - 1

Pore Volume Injected (PV)	Oil Recovery (%)
0.2	2.81 %
0.4	11.16 %
0.6	16.73 %
0.8	20.90 %
1	23.96 %
1.2	25.35 %
1.4	26.33 %
1.6	27.58 %
1.8	28.83 %

4.8.2 Core Flood – 2:

Second core used was also limestone with the same dimensions but pore volume was 64.32 cc. Porosity was also high for this core that was 0.1897. Permeability was measured in the same fashion for this core also with the same flow rates and using the same equation and it turned out to be 73 mD. Figure 4-57 shows the plot for Darcy Law to calculate the permeability of core sample using brine. The core was then saturated with oil and aging was done for 15 days. S_{wi} for this core was reduced to 34.7% leaving 22.32cc formation water behind in the core with 42cc oil. After 15 days aging, the core flooding was started. The temperature in this experiment was kept at 90^{o}C for the whole experiment.

Water flooding using brine was started as a first step. Salinity used was 57,000 ppm and the flow rate was 0.5 cc/min. As water was injected, oil recovery started and by flowing 1.5 PV of brine, 38% oil was recovered. Major recovery was achieved after 0.3 PV of water flooding but still oil was coming in small amount. After 1.5 PV, oil recovery was fully stopped and only brine was coming out.

In the second step, SP flooding was started with 0.2% Marlipal and 0.25% HPAM. 1.2 PV of the SP solution was used to achieve 26.43% oil recovery. As Marlipal is non-ionic in nature and was not able to give ultralow IFT, it was not able to change the wettability of the rock. For this reason when in the third step brine was injected again, no oil was recovered. Still Marlipal showed promising results of increasing the oil recovery up to 26.43%. Figure 4-58 shows the results of cumulative oil recovery against each 0.1 PV injected. Table 4-2 shows the results for each 0.1 PV injected of the SP solution.

From the core flooding experiments it is concluded that both Alfoterra and Marlipal showed promising results. Oil recovery increase was much higher and economically, cost of chemicals can be compensated when this much recovery will be achieved. Marlipal along with HPAM was able to produce 26.43% oil and Alfoterra in combination with HPAM produced 28.83% oil which is a significant increase in the oil recovery. Both of the SP systems are eligible to be used in the field.

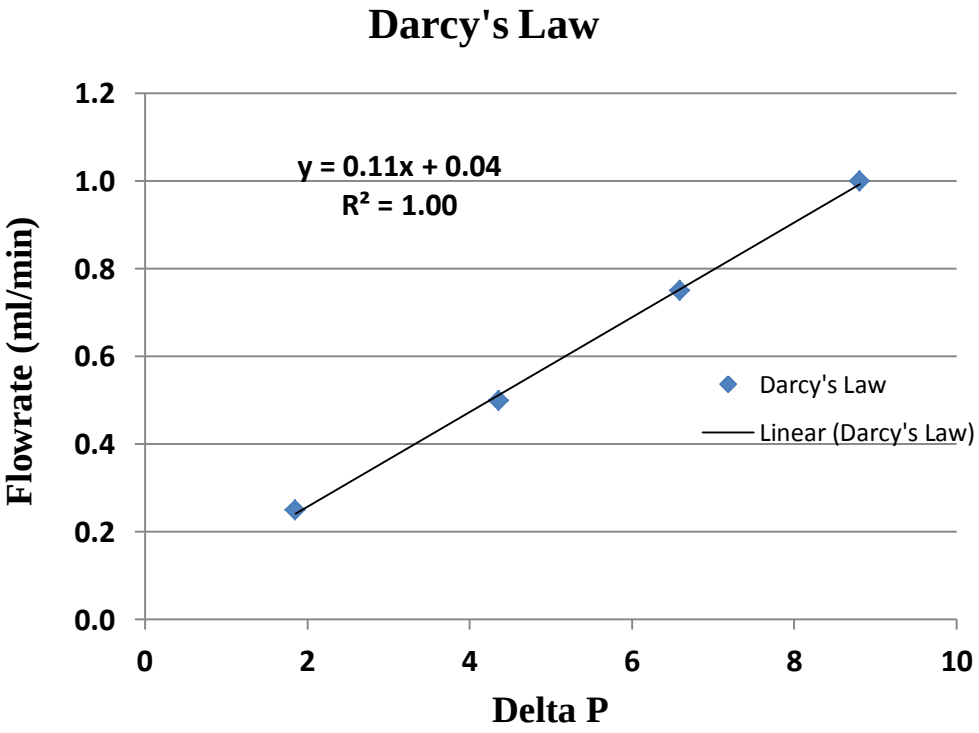

Figure 4-57 Formation water flow rate vs pressure drop for permeability calculations in Core Flood - 2

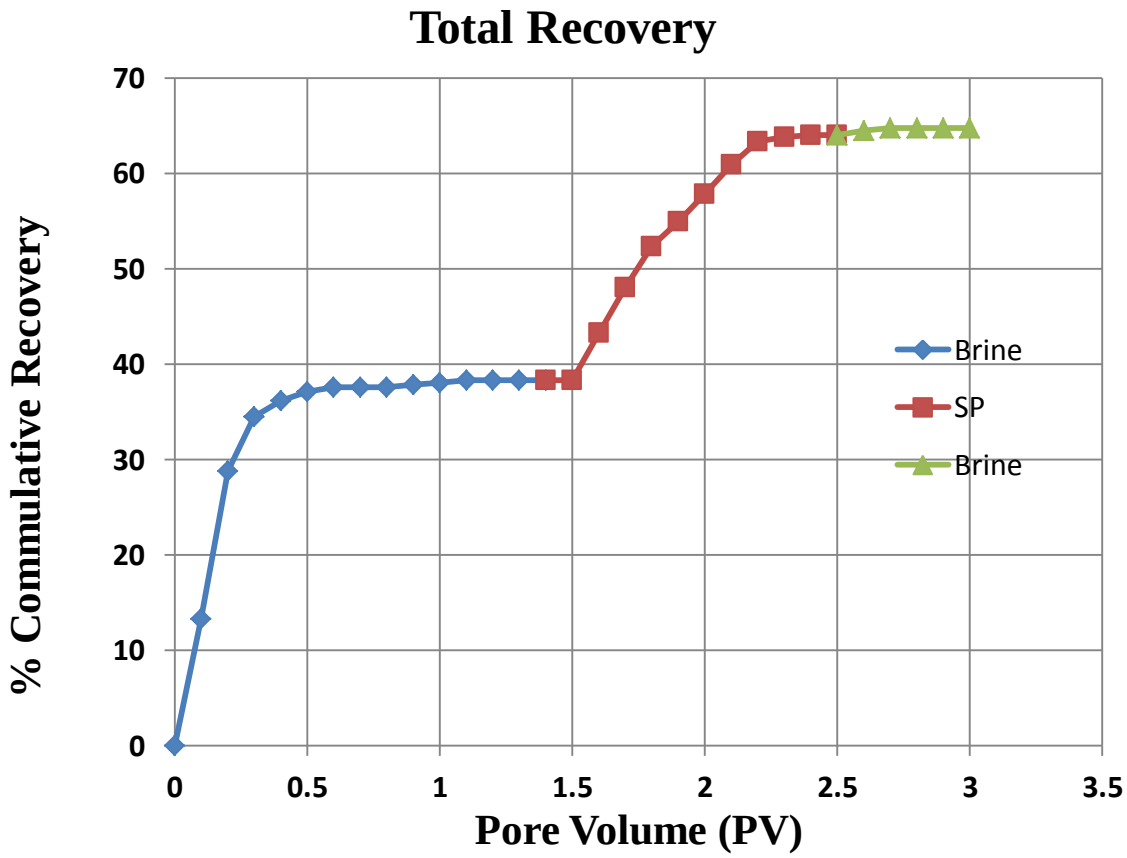

Figure 4-58 % recovery after brine and SP Flooding in Core Flood - 2

Table 4-2 Oil recovery % for different pore volume injections of SP in Core Flood - 2

Pore Volume Injected (PV)	Oil Recovery (%)
0.1	5.00 %
0.2	9.76 %
0.3	14.05 %
0.4	16.67 %
0.5	19.52 %
0.6	22.62 %
0.7	25.00 %
0.8	25.48 %
0.9	25.71 %
1	25.71 %
1.1	26.19 %
1.2	26.43 %

CONCLUSION

Surfactant – Polymer (SP) system was examined to evaluate its performance in cEOR and it showed promising potential in cEOR for carbonate reservoirs. Ethoxylated and Propoxylated surfactants were used in combination with HPAM. The polymer was added to displacing fluid to increase the viscosity and enhance sweep efficiency. Sweep efficiency could be increased either by increasing the viscosity of solution or decrease interfacial tension between solution and oil. Different surfactants were used to lower the IFT. The main results obtained and conclusions from different techniques are as follows:

- HPAM increased viscosity of DIW but in the presence of salts the viscosity was decreased. Still the viscosity was higher than the viscosity of water by ten times. The decrease in the viscosity was observed due to charge shielding effect.
- Marlipal O13/120 as non-ionic in nature did not affect the bulk viscosity. Alfoterra 123-8s was anionic in nature. The viscosity of the HPAM solution was decreased as the concentration of Alfoterra was increased.
- The storage modulus was also not affected from Maripal. Alfoterra decreased storage modulus as its concentration was increased.
- SP solutions were tested in presence of salts. Charge shielding effect reduces the viscosity but still it was higher than the viscosity of water by ten times.
- Marlipal was found to be thermally very strong. The surfactant was tested for short and long period aging and its shows promising results when analyzed through TGA, FTIR and NMR. For short period aging Marlipal was stable up to 190^{o}C. In long period aging Marlipal was aged at 90^{o}C for a week and it remained stable and showed

promising results in NMR and FTIR. For high temperature applications, Marlipal produced promising results.

- Alfoterra was stable when aged for short period and it was stable up to 180^{o}C. When aged at 90^{o}C for 24 hours, Alfoerra showed visible physical degradation. Different spectra obtained from FTIR and NMR confirmed the degradation. Major degradation was breakage of double bonds present in the structure. Alfoterra could be used in low temperature applications.
- Marlipal was unable to give ultralow IFT values even in presence of salts. Alfoterra gave low IFT with DIW but with sea water it was able to give ultralow IFT values. Optimum concentration for Alfoterra was found to be 0.3% in presence of salts where it produced ultra-low IFT at low temperatures. Alfoterra was able to give ultra-low IFT at high temperatures when co-surfactant was added in the solution.
- Phase behavior experiments showed that Marlipal was unable to produce Type-III micro-emulsion. Alfoterra produced micro-emulsion when its concentration was fixed at 0.3% and salinity was 30,000 ppm.
- In adsorption experiments, major adsorption was observed for sulfate ions and calcium ions were desorbed. Almost similar results were obtained in case of both surfactants.
- Indiana Limestone was used to carry out core flooding experiments. Core was 12 in long and had 1.5 in diameters. The optimum concentration of Alfoterra was 0.3% used in combination with 0.25% HPAM. It was able to enhance the oil recovery by 42%. In second experiment, 0.2% Marlipal was added to 0.25% HPAM solution and this SP system recovered 38% oil.

- With Alfoterra and HPAM recovery was increased up to 71.28% but it changes the wettability of rock. When sea water was flooded again after SP flooding, recovery was increased up to 82%. Only 1.7 PV of the SP solution was used for this experiment.
- Marlipal was able to increase the recovery up to 64.76%. As Marlipal was not able to change the wettability no oil was recovered when sea water was flooded after SP flooding. 1.2 PV of the SP solution was consumed during SP flooding.
- Both systems showed promising potential for oil recovery and both could be used for different conditions. Marlipal will be preferred for high temperature applications and Alfoterra will be preferred for high salinity application.

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